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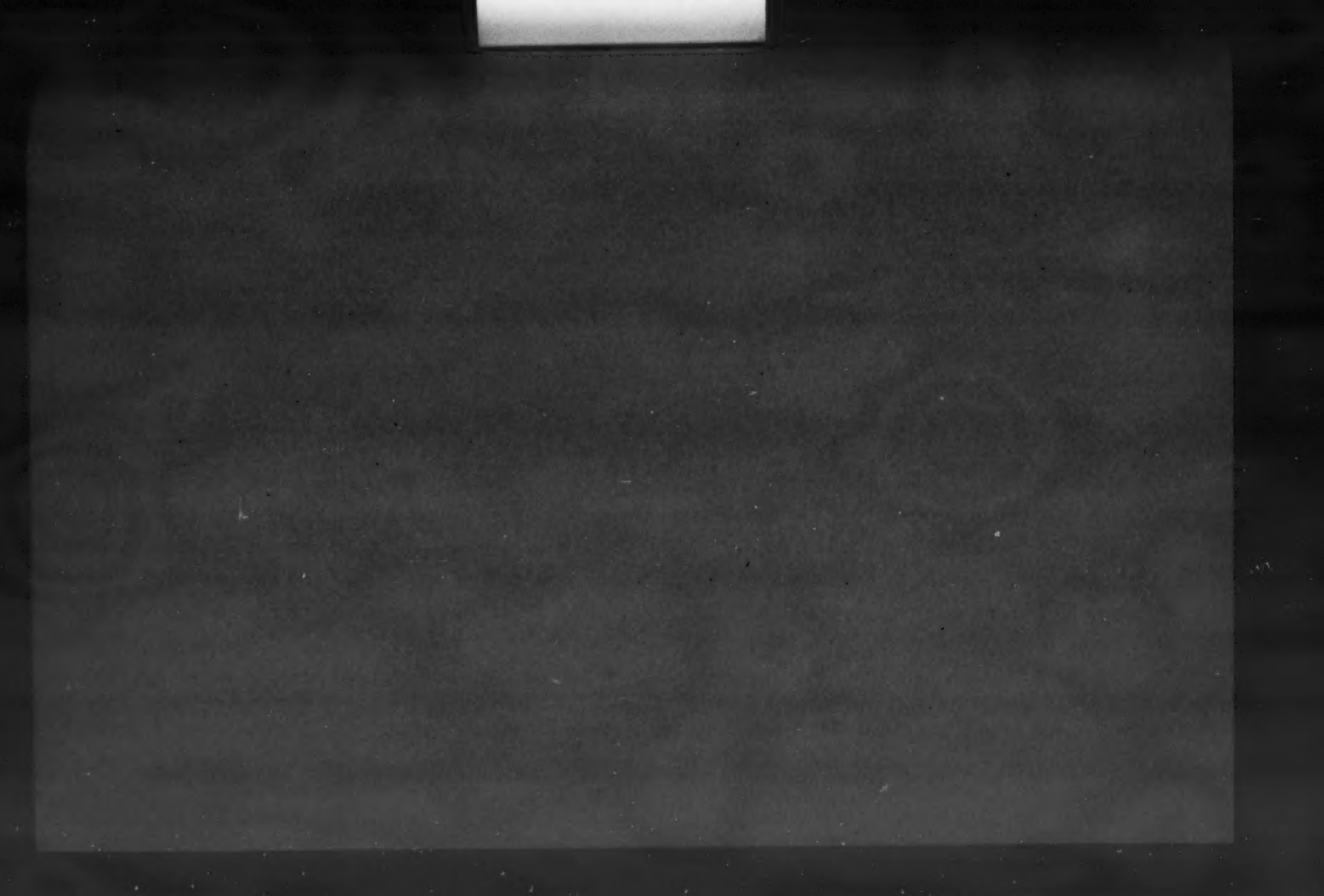

Vol. III, No. 6, Section B of the "Proceedings of the Indian Academy of Sciences" will be issued as a special number along with Vol. IV, No. 1.

# LIPINS OF FENUGREEK (*TRIGONELLA FOENUM GRAECUM.*)

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AND
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Received May 3, 1936.

Fenugreek, extensively cultivated throughout India and Egypt, forms an essential constituent of the Indian, Arab and Egyptian dietary. Data relating to the area under its cultivation in India are not available but statistics show that the seeds are exported to the extent of about 770 tons per annum valued at about 2 lakhs and a half—(1927), principally to Arabia, Egypt and Italy. Its nutritive value has long been recognised, aqueous extracts of the seed being commonly administered to anæmic and ricketty children. Dr. Blum (1927) states that fenugreek can be employed as a substitute for cod liver oil in cases of lymphatism, scorfula, rickets, anæmia and debility following infectious diseases or neurasthenia as well as in gout and diabetes in which it may be combined with insulin.

The seeds are valued for their tonic, astringent, emollient and aphrodosiac properties and recently their dietetic value is being more widely accepted. Andre (1932) reports an augmentation in the weight of adults (1·5 to 4 kg.) in 1–2 months by administering the powder to them in 2–3 gm. doses before food. Fenugreek is given to women after parturition in the form of powder or a decoction sweetened with sugar, for re-establishing original weight and improving lactation. It constitutes an essential ingredient of pills and powders administered for the treatment of diabetes mellitus ; it also acts as a safe nutrient in cases of diabetes.

Reutter (1927) has noted the presence of several bases such as choline, trigonelline, methylamine, neurine and betain, which possibly result during the hydrolysis of the lipins associated with the grain. The seed contains about 7 per cent. of a fixed oil (1919), bright yellow in colour, with a characteristic odour and taste. Wunschendorff (1919) has found that the oil possesses an iodine value of about 137, contains 6·25 per cent. of a lecithin and has a phosphorus content of ($P_2O_5$) 0·55 per cent. In a further communication (1919) he has reported the presence of a saponin, readily soluble in water and easily hydrolysed by dilute acids yielding dextrose.

Jahns (1885) isolated an akaloid, trigonelline, from the seeds by exhausting them with 70 per cent. alcohol. 0·14 per cent. of a light brown neutral volatile oil possessing the distinct odour of seeds has been described (1903). The preliminary study of the proteins of the seed has been conducted by Wunschendorff (1919) who has isolated 25 per cent. of a globulin, 20 per cent. of two albumins and 55 per cent. of an alkali soluble nucleoproteid having a specific lævo rotation of $[\alpha]_D = -97·7°$. More recently, the albumins and globulins have been examined in greater detail by Sreenivasa Rau and Sreenivasaya (1932) while a preliminary examination of the prolamin, " Helbin ", has been conducted by Hassan and Basha (1932), a more complete study of which has been carried out by Sreenivasa Rau, Sastri and Narayana (1933).

The mucilage to which the emollient properties are attributed, is described to be a silico-phosphoric acid ester of mannogalactan (1932) in contradiction to the previous finding of Bourquelot and Herissey that it is a mannogalactan (1900). A critical examination of this question by Hariharan and Sastri (1933) has revealed that the mucilage is a simple mannogalactan.

It will be observed from the foregoing review of the work done on Fenugreek that there have been no systematic studies on the lipins of the seed to which the reputed tonic properties of the seed may largely be due. A detailed investigation of lipins has accordingly been undertaken in our laboratories and the present communication deals with the methods employed in the isolation, fractionation and chemical characterisation of the lipins.

*Experimental.*

The seeds, on crushing, separate roughly into two portions, a yellow flour which is easily powdered and a residue consisting of the snow-white gelatinous endosperms which cannot be ground. The yellow meal has a nitrogen value of 4·54 per cent. while the endosperm fraction, constituting the source of the mucilage, if carefully separated, is found to contain practically no nitrogen. Table I gives the proximate composition of the yellow meal in percentages of moisture-free material.

TABLE I.

| Ether extract | 98% alcohol extract | 70% alcohol extract | Crude protein N × 6·3 | Total Ash | Total P | Total S | Starch |
|---|---|---|---|---|---|---|---|
| 8·1 | 4.9 | 11·2 | 29·9 | 3·5 | 0·62 | 0·003 | 2·1 |

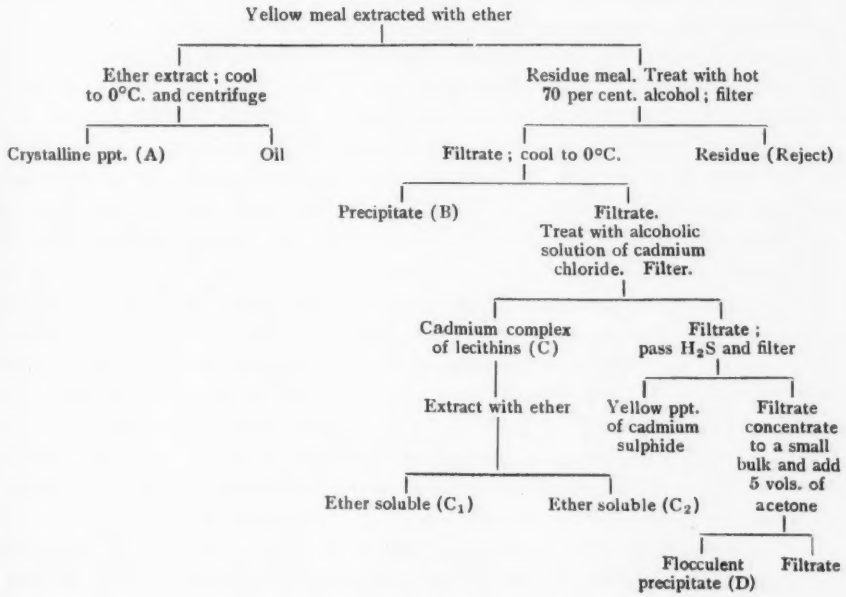
The nitrogen and phosphorus values of the ether extract are 0·38 and 0·52 per cent. respectively while the corresponding values for the alcohol

extract are (N) 1·10 and (P) 1·51 per cent., about thrice as high. About 3 per cent. of the total nitrogen and 30 of the total phosphorus of the yellow meal are extracted by successive treatments with ether and alcohol, while direct treatment with 70 per cent. alcohol, however, yields about 5·8 and 60 per cent. of the total nitrogen and phosphorus respectively.

The ether extract of the meal consists of a viscous semi-drying oil, golden yellow in colour. On cooling the oil deposits a white crystalline substance (A) which can be recovered by centrifuging and purified from the oil by washing with acetone in which the crystals are insoluble. The substance is sparingly soluble in ether and in absolute alcohol from which it could be recrystallised ; it is freely soluble in water and also in 70 per cent. alcohol from which it can be precipitated by adding 10 volumes of acetone. The purified product contains both nitrogen and phosphorus and represents the oil soluble phospholipin.

The ether extracted meal, on treatment with hot 70 per cent. alcohol, yields a clear light yellow solution which on cooling to 0° C. deposits a white precipitate (B) which can be filtered off and washed with cold alcohol. The filtrate is concentrated to a small bulk and treated with an alcoholic solution of cadmium chloride, to precipitate the true lecithins as double salt.

TABLE II.


Yellow meal extracted with ether
Ether extract ; cool to 0°C. and centrifuge
Residue meal. Treat with hot 70 per cent. alcohol ; filter
Crystalline ppt. (A)
Oil
Filtrate ; cool to 0°C.
Residue (Reject)
Precipitate (B)
Filtrate. Treat with alcoholic solution of cadmium chloride. Filter.
Cadmium complex of lecithins (C)
Filtrate ; pass $H_2S$ and filter
Extract with ether
Yellow ppt. of cadmium sulphide
Filtrate concentrate to a small bulk and add 5 vols. of acetone
Ether soluble ($C_1$)
Ether soluble ($C_2$)
Flocculent precipitate (D)
Filtrate

The mixture is centrifuged to recover the cadmium complex (C) and the centrifugate treated with hydrogen sulphide to remove excess of cadmium as sulphide which is filtered off. The filtrate is concentrated to a small bulk and 5 volumes of acetone added when a flocculent precipitate (D) is obtained. Table II gives a schematic representation of the various treatments given to the material for isolating the different fractions.

The nitrogen and phosphorus contents of the five fractions in percentages of the material as also their N : P ratios are given in Table III. $C_1$ represents the ether soluble portion and represents the cadmium compound

TABLE III.

| | A | B | $C_1$ | $C_2$ | D |
|---|---|---|---|---|---|
| Nitrogen .. | + | 0·75 | 0·58 | 0·96 | 1·08 |
| Phosphorus .. | + | 0·78 | 1·32 | 0·68 | 0·06 |
| N : P .. | .. | 2·5 : 1 | 1 : 1 | 3 : 1 | .. |

of the true lecithin, a striking confirmation of which is obtained by the analytical data presented in Table III. B corresponds in composition to sphingomyelin. Fraction D contains nitrogen, is strongly hygroscopic, and freely soluble in water from which it can be reprecipitated by the addition of 10 volumes of absolute alcohol or acetone. The product has a very low content of phosphorus which can be eliminated by further purification. All attempts at obtaining crystalline substances from the crude product have so far been unsuccessful. The crude product is optically active, contains sulphur and on hydrolysis with dilute acids readily splits off a reducing sugar which has been identified as galactose both by its osazone and mucic acid tests.

A further fractionation of the crude galactolipins was carried out by dissolving the product in pyridine in which it was only partially soluble. The pyridine insoluble fraction was kept separate and the pyridine soluble portion was fractionally precipitated by successive additions of chloroform, yielding four fractions, *a*, *b*, *c*, *d*. These were purified by dissolving in dilute alcohol and precipitating with anhydrous acetone. An analysis of these fractions as also those of the crude product and the pyridine insoluble fraction is presented in Table IV.

The analytical data of the above four fractions, *a*, *b*, *c* and *d*, point to the conclusion that the pyridine soluble fraction consists mainly of two

TABLE IV.

| | Crude product D | Pyridine insoluble fraction | Pyridine soluble | | | |
|---|---|---|---|---|---|---|
| | | | *a* | *b* | *c* | *d* |
| $[\alpha]_D^{25°C.}$ original product .. | 31·58 | 91·22 | 67·1 | 28·73 | —17·56 | —22·22 |
| „ after acid hydrolysis .. | 21·05 | 28·01 | 22·0 | 10·85 | —2·42 | 0·00 |
| Nitrogen, N .. | 1·08 | 1·67 | 1·38 | 0·34 | 0·15 | 0·26 |
| Phosphorus, P .. | 0·06 | 0·21 | 0·07 | 0·03 | 0·01 | 0·01 |
| Sulphur, S .. | 0·12 | 0·26 | .. | .. | .. | .. |
| Galactose .. | 32·89 | 38·42 | 43·01 | 37·55 | 26·33 | 31·14 |

substances, a dextro component predominent in fraction *a*, and a lævo component comprising the fraction *d*. Emulsin acts on both *a* and *d*, indicating thereby that the fractions contain glycosides.

The pyridine insoluble fraction is interesting because of its sulphur content and is being subjected to further investigation.

*Summary.*

1. A preliminary study of the lipins of Fenugreek seeds has been made. Methods for the isolation and fractionation of the lipins are described in detail.

2. A phospholipin allied to sphingomyelin, an oil soluble true lecithin which forms a complex with cadmium salts, a pyridine soluble galactolipin and a galactoside and a pyridine insoluble galactolipin containing sulphur are among the most interesting fractions that have been isolated from the seeds.

3. A detailed investigation of the cadmium complex and the pyridine insoluble galactolipin is under progress.

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# ULTRASONIC VELOCITIES IN ORGANIC LIQUIDS.

## Part IV. Halogen Compounds.

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Received May 22nd, 1936.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

### *1. Introduction.*

Part I of this series contained determinations of ultrasonic velocity in a number of halogen compounds, mainly of the aliphatic class. Therein it was observed, that in general, introduction of one or more heavy atoms such as bromine, tended to bring down the velocity in the compound. The lowest recorded was that for carbon tetrachloride, being 928 metres per second at 23° C.

It was thought worthwhile to make such determinations for some more halogen compounds and investigate the influence of substitution on sound velocity.

In Parts I, II and III, the frequency of vibration was taken as that set up initially, the apparatus not being disturbed as one liquid was substituted for another. The experimental arrangement was identical for every liquid studied; and the quartz crystal was just suspended on top of the liquid. Whereas, in this series, it was found necessary at times to tune up the circuit and to determine for every liquid the frequency of oscillation. This was done by means of a Precision wave-meter. Though there was not much difference in the frequency for identical conditions of experimentation, from one liquid to another, it should be emphasised that this method eliminated any possible uncertainty in the frequency.

### *2. Results.*

The following table gives determinations of ultrasonic velocity in several halogen compounds. The last column gives the values for adiabatic compressibility for these compounds as calculated from their sound velocities and from separate determinations carried out of their densities as well.

The frequency of oscillation employed was about $7 \cdot 32 \times 10^6$ c./s.

TABLE I.

*Ultrasonic Velocities in Halogen Compounds at about* $7 \cdot 32 \times 10^6$ *c./s.*

| | Liquids | Chemical Formula | Temp. in °C. | Density | Velocity of sound in metres per second | Adiabatic compressibility $\beta_\phi \times 10^6$ |
|---|---|---|---|---|---|---|
| 1 | Ethyl bromide .. | $C_2H_5Br$ | 28° | 1·428 | 892 | 88·1 |
| 2 | Butyl bromide (*n*) .. | $CH_3.(CH_2)_2.CH_2Br$ | 25°·5 | 1·272 | 1016 | 76·2 |
| 3 | Butyl iodide (*n*) .. | $CH_3.(CH_2)_2.CH_2I$ | 28° | 1·616 | 959 | 67·3 |
| 4 | Allyl chloride .. | $CH_2 : CH.CH_2Cl$ | 28° | 0·937 | 1088 | 90·1 |
| 5 | Acetylene dichloride (*cis*).. | $CHCl : CHCl$ | 25°·5 | 1·262 | 1025 | 75·4 |
| 6 | Acetylene tetrachloride .. | $CHCl_2.CHCl_2$ | 28° | 1·578 | 1155 | 48·6 |
| 7 | Acetylene tetrabromide .. | $CHBr_2.CHBr_2$ | 28° | 2·962 | 1007 | 33·3 |
| 8 | Tetrachlorethylene .. | $C_2Cl_4$ | 28° | 1·623 | 1027 | 58·4 |
| 9 | Dichlorobenzene-*o* .. | $C_6H_4Cl_2$ | 28° | 1·294 | 1246 | 49·7 |
| 10 | Dichlorobenzene-*m* .. | ,, | 28° | 1·285 | 1232 | 51·2 |
| 11 | Benzoyl chloride .. | $C_6H_5.COCl$ | 28° | 1·211 | 1318 | 47·5 |
| 12 | Benzyl chloride .. | $C_6H_5.CH_2Cl$ | 28° | 1·102 | 1377 | 47·8 |
| 13 | Chlorobenzene .. | $C_6H_5.Cl$ | 23° | 1·101 | 1302 | 53·6 |
| 14 | Bromobenzene .. | $C_6H_5.Br$ | 28° | 1·495 | 1134 | 52·0 |
| 15 | α-Monochlornaphthalene | $C_{10}H_7.Cl$ | 27° | 1·189 | 1462 | 39·3 |

### 3. *Discussion.*

No data on acoustic velocity are available for the compounds studied in this paper.

We observed in earlier papers that acoustic velocities were lowered generally by the introduction of a heavier atom in place of a lighter one. As examples, we quote chloroform and bromoform, methylene halides and ethylene halides. The results of this paper in addition to confirming the view above mentioned, bear out also the effect of double bonds on the velocity. We shall now elaborate our points.

*Ethyl and butyl bromides.*—These bromides show low acoustic velocities compared with other ethyl and butyl compounds. The higher velocity in butyl bromide, as between these two, is due to the greater length of the molecule ; and such an effect due to the length of the chain has been noticed

before. Compared with their corresponding alcohols (Part I), the bromides have decidedly lower velocities, due to the introduction of a heavy atom of bromine, in place of .OH.

Ethyl bromide has a velocity of 892 metres/second at 28°C., the lowest so far known in liquids.

*Butyl halides.*—For the same length of the molecule, but with a heavier atom, such as iodine, the acoustic velocity is lowered. This is exemplified in butyl iodide which shows lower velocity than butyl bromide. The adiabatic compressibility for the former compound is smaller than that for butyl bromide.

*Acetylene chlorides.*—The sound velocities in acetylene dichloride and acetylene tetrachloride have been determined. We should ordinarily expect the tetrachloride to possess lower velocity, as it contains two more chlorine atoms. But surprisingly enough, the dichloride gives 1025 m./s. at 25°. 5 C. and the tetracholride 1155 m./s. at 28° C. This is in spite of the lower density of the dichloride. This can be explained only by the fact that the dichloride is unsaturated, having a double bond, while the tetrachloride is fully saturated. We should presume, therefore, that unsaturation favours lowering of sound velocity ; and other such instances will be quoted elsewhere.

Here may be compared the velocity in ethylene chloride $C_2H_4Cl_2$—a saturated compound—, which is 1240 m./s. at 23° C.

*Acetylene tetrahalides.*—The velocity in tetrabromide of acetylene is less than that in the tetrachloride by about 150 metres at 28° C. The observation holds good here, of heavy atom lowering the velocity. The adiabatic compressibility for the tetrabromide is less than that of the tetrachloride.

*Allyl chloride.*—Such a low velocity as was observed for this compound, is due to the presence of both a double bond and a chlorine atom.

*Tetrachlorethylene.*—That the presence of a double bond favours lower velocity is here again confirmed. Acetylene tetrachloride contains the same number of chlorine and carbon atoms (though 2 more hydrogen atoms) as tetrachlorethylene, but the sound velocity is more by 100 metres at 28° C. This is due to the adiabatic compressibility for $C_2Cl_4$ being greater. The only possible explanation seems to be that the double bond, present in $C_2Cl_4$, is responsible for these effects.

*Dichlorobenzenes.*—We observed earlier that in general, the ortho-substituted compound shows slightly higher acoustic velocity. This is also the case with the dichlorobenzenes, the ortho-dichlorobenzene having higher sound velocity.

Comparison can be made of the velocity in chlorobenzene, which contains only one chlorine atom. The velocity in it was found to be 1302 m./s. at 23° C. and making allowance for diminution in it for higher temperature (28° C.), the velocity is still higher than those for the dichlorobenzenes. A greater number of heavier atoms in the molecule decreases the velocity.

*Bromobenzene.*—The velocity in this compound is only 1134 metres/second at 28° C., which is very low for an aromatic liquid. This is much lower than that for chlorobenzene, as is to be expected on the introduction of a heavy atom. The density for bromobenzene is much higher than that for chlorobenzene, while the adiabatic compressibility is only slightly less.

It may be remarked here that bromobenzene has a velocity much lower than that for any of the dichlorobenzenes, by nearly 100 metres at 28° C. But the adiabatic compressibilities for these compounds are about the same.

*Benzyl and Benzoyl chlorides.*—Benzyl chloride has a velocity of 1377 metres/second while the other has 1318 metres/second both at 28° C. The higher velocity in the former compound is explained by the fact that it possesses lower density, with a compressibility nearly equal to that of the latter compound.

*α-Monochlornaphthalene.*—This compound gives an acoustic velocity of 1462 m./s. at 27° C. Freyer, Hubbard and Andrews,[2] in their paper, have determined in the analogous bromine compound the sound velocity and they give it for 414 kc., as 1350 m./s. at 27° C. This is definitely lower than that for the chlorine compound and what has been so often said regarding the substitution of a heavy atom, here again finds confirmation.

It is a pleasure to thank Sir C. V. Raman, Kt., F.R.S., N.L., for his interest in the work.

## 4. *Summary.*

The paper gives ultrasonic velocities at about $7 \cdot 32 \times 10^6$ c./s., and adiabatic compressibilities calculated therefrom, in 15 halogen substituted compounds, of both aliphatic and aromatic series. It is found in general, from a consideration of the results, that (1) introduction of a heavier atom lowers acoustic velocity, and (2) the presence of a double bond—or unsaturation—favours lowering of the velocity.

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# UPON SOME NEW RESULTS IN THE DOMAIN OF NON-LINEAR MECHANICS.

By Prof. Dr. N. Kryloff
and
Prof. Dr. N. Bogoliüboff, Kieff, URSS.

Received May 5, 1936.
[Extract from a letter to Prof. D. D. Kosambi.]

Although our methods could be applied to the general case $\phi = \phi(x, y, t)$ (provided $\phi$ is relatively small with respect to $n$), we shall treat in what follows only the case when $\phi = p \sin qt$, the value of $p$ being sufficiently small as compared with $n$.

We shall obtain for this case the first approximation. The relative error in periods will be of the order of magnitude of $\left(\frac{p}{n}\right)^2$.

In the equations

$$(1)\quad \frac{d^2x}{dt^2} + n^2x = p \sin qt \frac{dy}{dt}; \qquad \frac{d^2y}{dt^2} + n^2y = -p \sin qt \frac{dx}{dt}$$

we shall suppose first that $n$ is sufficiently near to $\frac{r}{s}q$, $r$ and $s$ being some mutually prime integers.

Let us change the variables (compare to the well-known method "de la variation des constantes arbitraires").

$$(2)\quad \begin{cases} x = a \sin \frac{r}{s} qt + b \cos \frac{r}{s} qt; \\ \frac{dx}{dt} = a \frac{r}{s} q \cos \frac{r}{s} qt - b \frac{r}{s} q \sin \frac{r}{s} qt; \\ y = \alpha \sin \frac{r}{s} qt + \beta \cos \frac{r}{s} qt; \\ \frac{dy}{dt} = \alpha \frac{r}{s} q \cos \frac{r}{s} qt - \beta \frac{r}{s} q \sin \frac{r}{s} q; \end{cases}$$

where $a$, $b$, $\alpha$, $\beta$ are new unknown functions of $t$.

By substituting these expressions in (I) we obtain after some evident computations the following system of equations equivalent to the primary system (I).

$$
(3)\quad \begin{cases}
\frac{r}{s}\,q\,\frac{da}{dt} = \Big[p\sin qt\,\Big\{\alpha\,\frac{r}{s}\,q\cos\frac{r}{s}\,qt - \beta\,\frac{r}{s}\,q\sin\frac{r}{s}\,qt\Big\} \\
\qquad + \Big\{\Big(\frac{r}{s}\,q\Big)^2 - n^2\Big\}\,\Big\{a\sin\frac{r}{s}\,qt + b\cos\frac{r}{s}\,qt\Big\}\Big]\cos\frac{r}{s}\,qt\,; \\
\frac{r}{s}\,q\,\frac{db}{dt} = -\Big[p\sin qt\,\Big\{\alpha\,\frac{r}{s}\,q\cos\frac{r}{s}\,qt - \beta\,\frac{r}{s}\,q\sin\frac{r}{s}\,qt\Big\} \\
\qquad + \Big\{\Big(\frac{r}{s}\,qt\Big)^2 - r^2\Big\}\,\Big\{a\sin\frac{r}{s}\,qt + b\cos\frac{r}{s}\,qt\Big\}\Big]\sin\frac{r}{s}qt\,; \\
\frac{r}{s}\,\frac{d\alpha}{dt} = \Big[-p\sin qt\,\Big\{\alpha\,\frac{r}{s}\,q\cos\frac{r}{s}\,qt - b\,\frac{r}{s}\,q\sin\frac{r}{s}\,qt\Big\} \\
\qquad + \Big\{\Big(\frac{r}{s}\,q\Big)^2 - n^2\Big\}\,\Big\{\alpha\sin\frac{r}{s}\,qt + \beta\cos\frac{r}{s}\,qt\Big\}\Big]\cos\frac{r}{s}qt\,; \\
\frac{r}{s}\,\frac{d\beta}{dt} = -\Big[-p\sin qt\,\Big\{a\,\frac{r}{s}\,q\cos\frac{r}{s}\,qt - b\,\frac{r}{s}\,q\sin\frac{r}{s}\,qt\Big\} \\
\qquad + \Big\{\Big(\frac{r}{s}\,q\Big)^2 - n^2\Big\}\,\Big\{\alpha\sin\frac{r}{s}\,qt + \beta\cos\frac{r}{s}\,qt\Big\}\Big]\sin\frac{r}{s}qt.
\end{cases}
$$

We see at once that these equations are of the form

$$\frac{dx_\kappa}{dt} = X_\kappa\ (x_1, \cdots\cdots x_n\,;\, t),\ k = 1, 2\cdots\cdots n,$$

where the right-hand parts are sufficiently small and periodic $\Big($with a period $\tau = \frac{2\pi s}{q}\Big)$ with respect to $t$.

In order to obtain the first approximation of the system of such a kind we have established a principle, which we have called—the *Averaging Principle.*

According to this Principle for the obtaining of the first approximation we may average the right-hand members of (4) with respect to $t$ (during this averaging $x_1, x_2, \ldots . x_n$ must be considered as constants). Hence instead of (4) we obtain the following equations of the first approximation:

$$\frac{dx_\kappa}{dt} = \frac{1}{\tau}\int_0^\tau X_\kappa\ (x_1, x_2, \cdots\cdots x_n, t)\,dt\,;\ \kappa = 1, 2\cdots\cdots n.$$

By applying this tool to the system (3) we get in the case when $\frac{r}{s} \neq \frac{1}{2}$ $\Big($that is if $n$ is not near to $\frac{q}{2}\Big)$:

$$2\,\frac{r}{s}\,q\,\frac{da}{dt} = \Big[\Big(\frac{r}{s}\,q\Big)^2 - n^2\Big]\,b\,; \qquad 2\,\frac{r}{s}\,q\,\frac{db}{dt} = -\Big[\Big(\frac{r}{s}\,q\Big)^2 - n^2\Big]\,a\,;$$

$$2\,\frac{r}{s}\,q\,\frac{d\alpha}{dt} = \Big[\Big(\frac{r}{s}\,q\Big)^2 - n^2\Big]\,\beta\,; \qquad 2\,\frac{r}{s}\,q\,\frac{d\beta}{dt} = -\Big[\Big(\frac{r}{s}\,q\Big)^2 - n^2\Big]\,\alpha.$$

But neglecting the square $\left[n - \frac{r}{s}\,q\right]^2$ we have

$$\left(\frac{r}{s}\,q\right)^2 - n^2 = \left(\frac{r}{s}\,q\right)^2 - \left[\frac{r}{s}\,q + \left(n - \frac{r}{s}\,q\right)\right]^2 \cong 2\,\frac{r}{s}\,q\left(\frac{r}{s}\,q - n\right)$$

and therefore we obtain approximately

$$a = \mathrm{A}\sin\left[\left(\frac{r}{s}\,q - n\right)t + \psi\right];\quad b = \mathrm{A}\cos\left[\left(\frac{r}{s}\,q - n\right)t + \psi\right];$$

$$\alpha = \mathrm{B}\sin\left[\left(\frac{r}{s}\,q - n\right)t + \theta\right];\quad \beta = \mathrm{B}\cos\left[\left(\frac{r}{s}\,q - n\right)t + \theta\right];$$

where A, B, $\psi$, $\theta$ are the constants of integration.

We thus have

$$x = \mathrm{A}\cos(nt + \psi);\quad y = \mathrm{B}\cos(nt + \theta)$$

and we see also that in the case where $n$ is not near to $\frac{q}{2}$ (case of *the non-resonance*) the first approximation gives for the period the value $\frac{2\pi}{n}$.

The corrections to this value being thus of the order of smallness of $\left(\frac{p}{n}\right)^2$ further approximations must be calculated in order to get an idea of the influence of $p$, $q$ on the value of the period. These further approximations for some analogous cases were detailed in our book *Les méthodes de la Mécanique non linéaire appliquées à la théorie des oscillations stationnaires* (Kieff, 1934).

Let us now return to the case where $\frac{r}{s} = \frac{1}{2}$, that is where $n \sim \frac{q}{2}$ (case of resonance). For this case the equations of the first approximation are :

$$q\frac{da}{dt} = [(\tfrac{1}{2}\,q)^2 - n^2]\,b - \frac{\beta pq}{4};$$

$$q\frac{db}{dt} = -[(\tfrac{1}{2}\,q)^2 - n^2]\,a - \frac{apq}{4};$$

$$q\frac{d\alpha}{dt} = [(\tfrac{1}{2}\,q)^2 - n^2]\,\beta + \frac{bpq}{4};$$

$$q\frac{d\beta}{dt} = -[(\tfrac{1}{2}\,q)^2 - n^2]\,\alpha + \frac{apq}{4};$$

where we may also put

$$(\tfrac{1}{2}\,q)^2 - n^2 \cong q\left(\frac{q}{2} - n\right).$$

The above system is a linear system with constant coefficients and its characteristic equation will be

$$\left(\lambda^2 + \delta^2 + \frac{p^2}{4}\right) = 0, \qquad \text{where, } \delta = \frac{q}{2} - n.$$

Hence

$$\lambda = \pm j\sqrt{\left(\frac{q}{2} - n\right)^2 + \left(\frac{p}{2}\right)^2}$$

The frequencies of $a$, $b$, $\alpha$, $\beta$ will be therefore

$$\pm\sqrt{\left(\frac{q}{2} - n\right)^2 + \left(\frac{p}{2}\right)^2}$$

and thence we obtain the frequencies of $(x, y)$

$$\frac{q}{2} \pm \sqrt{\left(\frac{q}{2} - n\right)^2 + \left(\frac{p}{2}\right)^2}$$

We also see that in this case, when $n$ is near to $\frac{q}{2}$ (resonance of demultiplication) the first order approximation of period is not equal simply to $\frac{2\pi}{n}$, as in the previous case, but :

$$\frac{2\pi}{\frac{q}{2} \pm \sqrt{\left(\frac{q}{2} - n\right)^2 + \left(\frac{p}{2}\right)^2}}$$

In this letter we have made only a brief sketch of the application of our methods to your very interesting problem.

A more detailed study with suitable demonstrations may constitute a subject of an extensive paper which we hope to write in the near future.

# THE RAMAN SPECTRA OF PROPYLENE AND ISO-BUTANE.

By R. Ananthakrishnan.
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Received May 11, 1936.
(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

## *1. Introduction.*

A careful and systematic study of the Raman spectra of the more simple organic and inorganic molecules, comprising the intensity and polarisation characters of the modified lines is obviously of great importance from the standpoint of thier chemical constitution. Investigations in this direction have been taken up by Cabannes and Rousset, Lenard Simons, Langseth, Trumpy and others, who have shown that the polarisation characters of the Raman lines in certain simple molecular types when interpreted in the light of Placzek's theory are in good agreement with the accepted chemical constitution, and enable definite decisions to be made in cases where the structure is uncertain or controversial. The present communication describes the results of the study of the Raman spectra of propylene and iso-butane.

## *2. Experimental.*

The gases were taken directly from commercial cylinders supplied by the Ohio Chemical and Manufacturing Co., Ltd. Propylene was labelled 99·5% pure, while the guaranteed degree of purity in the case of iso-butane was 99%. The gases were condensed in thick-walled pyrex glass tubes cooled in a bath of alcohol and carbon-dioxide snow, after being dried and rendered dust-free by passing successively over anhydrous $P_2O_5$ and a long plug of compressed cotton wool. The tubes were sealed off leaving sufficient space for the expansion of the liquids. The spectra were taken at the room temperature using a Hilger two-prism spectrograph of high light gathering power. A quartz mercury arc served as the source of illumination and was focussed on the Raman tube by a large glass condenser. The time of exposure to get an intense picture was about 50 hours using a slit width of ·05 mm. In order to determine the state of polarisation of the Raman lines a quartz double image prism with its axes horizontal and vertical was interposed between the slit of the spectrograph and the observation end of the Raman tube, and the horizontal and vertical components of the scattered radiation were photographed separately and simultaneously in the usual manner.

## *3. Results.*

In what follows, the polarisation characters of the various Raman lines are indicated by the letters P and D, the letters having the following significance :

$$P \ll \frac{6}{7} \quad : \quad D \approx \frac{6}{7}$$

The quantitative estimates of depolarisation require correction under two heads : (1) convergence of the incident light beam which tends to enhance the genuine depolarisation[1], (2) unequal losses of the two components of the scattered radiation by reflection at the prism faces whereby the vertical component loses more than the horizontal, thus producing an apparent increase in the depolarisation.

(*1*) *Propylene.*—Next to ethylene, propylene forms the simplest member of the olefine series of hydrocarbons, having the general formula $C_nH_{2n}$. However, although investigations in the cases of ethylene are quite numerous, the Raman spectrum of propylene does not appear to have been completely analysed.† Table I gives the complete analysis of the Raman spectrum of this substance in the region between λ 4046 and λ 5100 :

TABLE I.

*Raman Spectrum of Propylene $H_2C : CH.CH_3$.*

| No. | ν | Assignment | Int. | Poln. | No. | ν | Assignment | Int. | Poln. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 19930 | *e*—3008 | 2*b* | P | 22 | 21974 | *k*—2731 | 1 | P |
| 2 | 19948 | *e*—2990 | 0 | | 23 | 22018 | *e*— 920 | 6 | P |
| 3 | 20014 | *e*—2924 | 4 | P | 24 | 22358 | *e*— 580 (band) | ½*d* | D |
| 4 | 20052 | *e*—2886 | ½ | P | | | | | |
| 5 | 20082 | *e*—2856 | ½ | | 25 | 22506 | *e*— 432 | 4 | P |
| 6 | 20204 | *e*—2734 | 0 | P | 26 | 23058 | *k*—1647 | 8 | P |
| 7 | 21289 | *e*—1642 | 10*s* | P | 27 | 23295 | *k*—1410* | 4 | P |
| 8 | 21511 | *i*—3010 | 0*d* | | 28 | 23368 | *e*— 430 | 0 | P |
| 9 | 21518 | *e*—1420* | 5 | P | 29 | 23407 | *k*—1298* | 8 | P |
| 10 | 21595 | *i*—2921 | ½ | P | 30 | 23785 | *k*— 920 | 5 | P |
| 11 | 21618 | *k*—3087 | ½ | | 31 | 24273 | *k*— 432 | 2 | P |
| 12 | 21642 | *e*—1296* | 8 | P | 32 | 24286 | *o*—3013 | 0 | |
| 13 | 21694 | *k*—3011 | 6*b* | P | 33 | 24298 | *q*—3090 *o*—2995 | ½*d* | P |
| 14 | 21719 | *k*—2896 | 1 | P | | | | | |
| 15 | 21749 | *k*—2956 | 0 | | 34 | 24372 | *q*—3016 *o*—2921 | 2 | P |
| 16 | 21781 | *k*—2924 | 10 | P | | | | | |
| 17 | 21812 | *k*—2893 | 4 | P | 35 | 24392 | *q*—2996 | ½ | P |
| 18 | 21847 | *k*—2858 | 1 | P | 36 | 24406 | *o*—2887 | 1 | P |
| 19 | 21882 | *k*—2823 | ½ | P | 37 | 24429 | *p*—2924 | 2 | P |
| 20 | 21910 | *k*—2795 | 0 | | 38 | 24462 | *q*—2926 | 4 | P |
| 21 | 21942 | *k*—2763 ? | 00 | | | | | | |

[1] R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, A, 1935, **2**, 133.

† The Raman Spectrum of propylene has been studied by M. Bourguel (*C.R.*, 1932, **194**, 1736) who has reported the following frequencies:—

| $\Delta\nu$(cm.$^{-1}$) .. | 1295 | 1414 | 1647 | 3007 | 3086 |
|---|---|---|---|---|---|
| Int. .. | 6 | 3 | 6*v* | 3*br* | 4*Bd* |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $\Delta\nu$(cm.$^{-1}$) .. | 432 | 580 | 920 | 1297* | 1415* | 1648 | 2732 | 2763 | 2795 | 2823 | 2857 |
| Int. .. | 3 | ½*bd* | 6 | 8 | 4 | 10*s* | 1 | 00 | 0 | ½ | 1 |
| $\rho$ .. | P | D | P | P | P | P | P | | | P | P |
| $\Delta\nu$(cm.$^{-1}$) .. | 2890 | 2924 | 2956 | 2990 | 3010 | 3087 | | | | | |
| Int. .. | 4 | 10 | 0 | 1 | 6*b* | ½ | | | | | |
| $\rho$ .. | P | P | | P | P | | | | | | |

(*2*) *Iso-Butane.*—The Raman spectrum of iso-butane in the liquid state has been studied by Bhagavantam[2] and later by Kohlrausch and Köppl[3] with practically identical results. As will be seen from Table II, the author's results stand in good agreement with those of the above workers. The state of polarisation of the Raman lines is given in the last column.

TABLE II.

*Raman Spectrum of Iso-Butane* $H.C.(CH_3)_3$.

| Bhagavantam | Kohlrausch & Köppl | Author | | |
|---|---|---|---|---|
| | | $\Delta\nu$(cm.$^{-1}$) | Int. | $\rho$ |
| 372 (4*b*) | 370 (4*b*) | 370 | 4*b* | D |
| 436 (2*b*) | 438 (1) | 437 | 1 | P |
| 796 (10) | 794 (9) | 795 | 10 | P |
| 967 (5*b*) | 962 (4*b*) | 965 | 4*b* | D |
| | 1098 (½*b*) | | | |
| 1177 (5*b*) | 1168 (4*sb*) | 1170 | 4*b* | D |
| 1355 (4*b*) | 1322 (3*b*) | 1325 | 3*b* | D |
| 1453 (10*b*) | 1452 (7*b*) | 1452 | 7*b* | D |
| 2624 (1) | 2628 (0) | 2625 | ½ | P |
| 2720 (4) | 2718 (7*b*) | 2720 | 4 | P |
| 2777 (2) | 2778 (2) | 2780 | 2 | P |
| 2870 (10) | 2868 (14*b*) | 2870* | 15 | P |
| 2892 (2) | | 2890 | 2 | |
| 2910 (3) | 2906 (7) | 2908 | 5 | P |
| 2936 (3) | 2936 (4) | 2935 | 5 | P |
| 2962 (8) | 2959 (12) | 2960* | 10 | D (?) |

*4. Discussion of Results.*

(*1*) *Propylene* $H_2C:CH.CH_3$.—As might be expected from the high value of the depolarisation for the gas,[4] the Raman spectrum of liquid propylene shows an intense wing accompanying the unmodified Rayleigh lines.

[2] S. Bhagavantam, *Ind. Jour. Phys.*, 1931, **6**, 695.

[3] K. W. F. Kohlrausch and F. Köppl, *Z. f. Phys. Chem.*, 1934, **26**, 209.

[4] R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, A, 1935, **2**, 156.

However, no minimum of intensity is perceptible for the wing in the close vicinity of the Rayleigh line. The characteristic feature of the Raman spectrum of propylene is that almost all the Raman lines are quite sharp, and more or less well polarised. The intense and well-polarised Raman line at 1648 cm.$^{-1}$ represents the C = C oscillation, while the polarised Raman frequency at 920 cm.$^{-1}$ presumably arises from the C – C oscillation. The frequency at 432 cm.$^{-1}$ is much less polarised than the first two and is in all probability the transverse frequency of the carbon chain. These three frequencies represent thus the fundamental frequencies of the carbon atoms.

The Raman lines at 1297 cm.$^{-1}$ and 1410 cm.$^{-1}$ are to be attributed to (C – H) deformation vibrations. It is noteworthy, that unlike the broad and depolarised (C – H) $\delta$ frequency in the case of the saturated aliphatic hydrocarbons, these two lines are sharp and depolarised to an extent less than 6/7. The polarisation photograph clearly shows that while the vertical component is quite sharp, the horizontal components of these two frequencies are rather diffuse.

The large number of frequencies in the 3·5 $\mu$ region have their origin in the oscillations of the hydrogen atoms, and their intensities are distributed over a wide range. A depolarised Raman band extends in the interval between $\Delta\nu = 2924$ cm.$^{-1}$ and $\Delta\nu = 3010$ cm.$^{-1}$

(*2*) *Iso-Butane* H.C. $(CH_3)_3$.—A striking contrast is noticed when one compares the Raman spectra of propylene and iso-butane. Most of the lines in the latter spectrum are broad and many of them are badly polarised in contrast to the sharp and well-polarised lines of the former. This difference is perhaps due to the symmetry of the iso-butane molecule which causes many of the vibrations to be degenerate. The wings accompanying the Rayleigh line in the Raman spectrum of iso-butane are much less prominent than in the case of propylene in conformity with the low depolarisation of the vapour.[5]

The molecule of iso-butane can be designated by $ZXY_3$, Z and X being on the symmetry axis. The model has the symmetry $C_{3v}$, (analogous for instance to the molecule $H.CCl_3$) and possesses three totally symmetrical and three doubly degenerate vibrations, all the six being allowed in the Raman effect as well as in the infra-red. The normal vibrations of the model have been diagrammatically represented and discussed in some detail by Kohlrausch.[6] The following figures are reproduced from his paper.

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[5] R. Ananthakrishnan, *loc. cit.*

[6] K. W. F. Kohlrausch, *Z. f. Phys. Chem.*, B, 1935, **28**, 340.

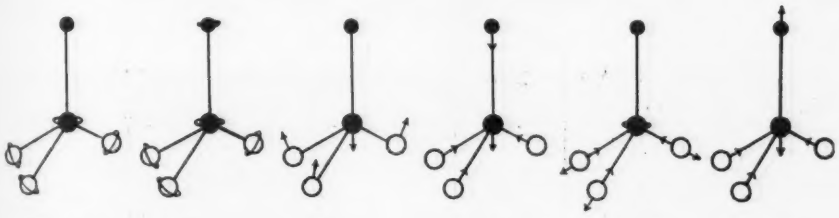


FIG. 1. Normal Vibrations of the $ZXY_3$ molecule.

The polarisation photograph of iso-butane shows at a glance that Kohlrausch's classification of the iso-butane frequencies requires revision. He gives the following classification :

$$\left.\begin{array}{lll} \omega_1 = \nu_1(CH_3) & = & 795 \text{ cm.}^{-1} \\ \omega_2 = \delta_3(CH_3) & = & 370 \quad ,, \\ \nu_4(H) & \approx & 3000 \quad ,, \end{array}\right\} \text{totally symmetric vibrations.}$$

$$\left.\begin{array}{lll} \omega_3 = \nu_{2,3}(CH_3) & = & 965 \quad ,, \\ \omega_4 = \delta_{1,2}(CH_3) & = & 437 \quad ,, \\ \delta_{4,5} & > & 1000 \quad ,, \end{array}\right\} \text{doubly degenerate vibrations.}$$

The Raman line at 437 cm.$^{-1}$ is well polarised, and hence cannot be the doubly degenerate frequency $\delta_{1,2}$. On the other hand, $\Delta\nu = 370$ cm.$^{-1}$ is highly depolarised and is presumably degenerate. These two frequencies have therefore to be interchanged in the above classification.

The Raman lines at 1170, 1325 and 1452 are all depolarised to the limiting value 6/7. From the fact that it occurs practically in all the saturated aliphatic hydrocarbons, we conclude that the depolarised line at 1452 cm.$^{-1}$ arises from the (C—H) $\delta$ vibration of the $CH_3$ group. Which of the two frequencies 1170 and 1325 is to be associated with $\delta_{4,5}$ is not clear from the polarisation measurements.

In the region of higher frequencies, there are no less than eight lines, showing a wide range of intensities. The polarisation photograph shows a remarkable feature in the case of the two intense lines at 2870 and 2960. In both cases, the vertical component is quite sharp, while the horizontal component is broad and diffuse. Presumably, there is a superposition of a polarised Raman line and a depolarised Raman band in these two cases. In the host of hydrogen frequencies, the identification of $\nu_4$ (H) is a matter of some difficulty. The following table gives a comparison of the Raman spectra of $H.CCl_3$ and $H.C.(CH_3)_3$ :—

TABLE III.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $H.C.Cl_3$ .. | $\Delta\nu$ | 259 | 364 | 664 | 756 | 1214 | 3016 |
| | $\rho$[7] | ·87 | ·19 | ·07 | ·86 | ·87 | ·20 |
| $H.C.(CH_3)_3$ .. | $\Delta\nu$ | 370 | 437 | 795 | 965 | 1325 | ? |
| | $\rho$ | D | P | P | D | D | |

Only the pertinent frequencies of iso-butane are included in the table. The similarity of the two spectra is strikingly brought out by the polarisation results.

In conclusion, the author wishes to express his respectful thanks to Professor Sir C. V. Raman for his kind interest and encouragement in the course of the present work.

## 5. *Summary.*

The Raman spectrum of propylene has been reported in detail and the observed frequencies are discussed in the light of the knowledge of their state of polarisation. The frequencies 1648, 920 and 432 are identified as the fundamental frequencies of the carbon chain, the first two being of the valence type, while the third one represents a deformation frequency. The fourteen additional lines are to be attributed to the oscillations of the hydrogen atoms. The Raman lines of propylene are characterised by extreme sharpness, and are more or less well polarised. The Raman spectrum of iso-butane forms a striking contrast, many of the lines being extremely broad and highly depolarised. It is suggestd that this difference might be due to the symmetry of the iso-butane molecule which causes many of the vibrations to be degenerate. An attempt has been made to interpret the spectrum of iso-butane with the help of the polarisation data. The close similarity between the Raman spectra of iso-butane and chloroform as revealed by polarisation studies is pointed out.

[7] L. Simons, *Comm. Phys.-Math. Soc. Scient. Fenn.*, 1932, **6**, 13.

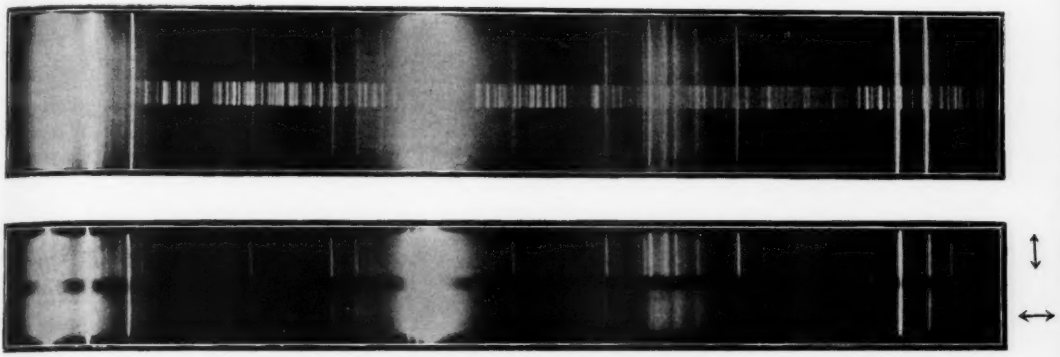

FIG. 2. Raman Spectrum of Propylene

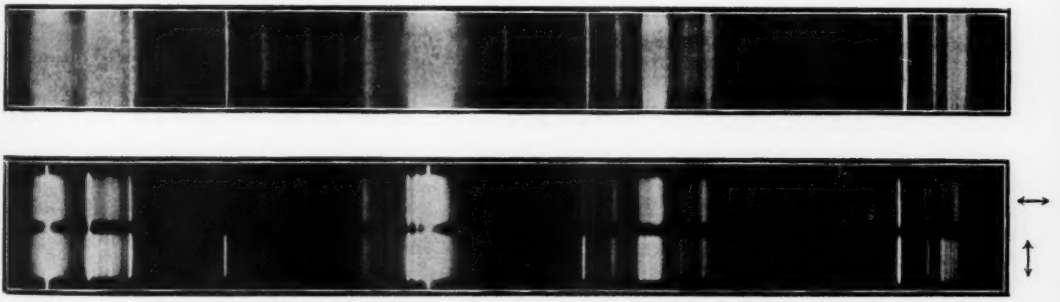

FIG. 3. Raman Spectrum of Iso-Butane

# THE RAMAN SPECTRA OF SELENIOUS ACID AND ITS SODIUM SALTS.

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Received May 28, 1936.
(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

## *1. Introduction.*

Recently in a note to *Current Science*[1] the author published the preliminary results of an investigation on the Raman spectrum of crystalline selenious acid. Then it was pointed out that the spectrum of the solid consists of not less than twelve sharp lines and is essentially different from that of its aqueous solution which has been reported on by Pringsheim and Yost.[2] To understand fully the significance of these lines in the solid, a detailed study of the problem has been undertaken and this report presents the results obtained both with the acid in the solid and molten states and in aqueous and alcoholic solutions and with the selenite and biselenite of sodium.

## *2. Experimental Method and Results.*

The experimental procedure was the same as has been described in the previous communications to these *Proceedings*. The substance used in this investigation was the anhydrous acid supplied by Kahlbaum. Fresh selenious acid prepared by the oxidation of selenium with concentrated nitric acid and purified by repeated recrystallisations from water gave an identical spectrum. The anhydrous acid shows a marked tendency to decompose on heating but the hydrated variety melts at about 70° C. to a light yellow liquid. For all purposes, this liquid is to be considered only as a solution of $H_2SeO_3$ in its water of crystallisation. It gave an intense spectrum with the 4358 radiations of the mercury arc ; but the 4047 line of the source was partially absorbed. The separation of amorphous selenium due to the action of light on the acid in the aqueous and alcoholic solutions gave rise to increased Tyndall scattering ; yet tolerably good pictures were obtained by carefully filtering the solutions several times through thick folds of filter paper.

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[1] Venkateswaran, C. S., *Current Science*, 1935, **4**, 309.

[2] Pringsheim and Yost, *Z. Physik*, 1929, **58**, 1.

The biselenite of sodium was prepared by titrating with a solution of sodium hydroxide using *p*-nitrophenol as indicator and the selenite by using thymolphthalein as indicator.

The spectrograms were measured by means of a Hilger Cross-slide microscope in comparison with an iron arc spectrum. The results are given in Tables I, II and III and the enlarged photographs of some of the spectra are reproduced in the accompanying plate.

TABLE I.

*$H_2SeO_3$ Crystal.* (*d* = 4047, *e* = 4077 *and h* = 4358.)

| No. | Raman lines | | $\Delta\nu$ cm.$^{-1}$ | Intensity | Assignment |
|---|---|---|---|---|---|
| | wave-length | wave-number | | | |
| 1 | 4047·0 | 24581 | 124 | 2 | *d* |
| 2 | 4088·3 | 24453 | 252 | 4 | *d* |
| 3 | 4094·0 | 24418 | 287 | 2 | *d* |
| 4 | 4096·0 | 24407 | 298 | 1 | *d* |
| 5 | 4107·0 | 24342 | 363 | 0 | *d* |
| 6 | 4120·5 | 24262 | 254 | 2 | *e* |
| 7 | 4126·1 | 24229 | 287 | 0 | *e* |
| 8 | 4134·5 | 24180 | 528 | 3*br* | *d* |
| 9 | 4146·8 | 24108 | 597 | 8 | *d* |
| 10 | 4166·1 | 23996 | 709 | 3 | *d* |
| 11 | 4179·4 | 23920 | 596 | 3 | *e* |
| 12 | 4197·3 | 23818 | 887 | 8 | *d* |
| 13 | 4195·9 | 23826 | 888 | 1 | *h* |
| 14 | 4201·1 | 23796 | 909 | 2 | *d* |
| 15 | 4206·9 | 23764 | 941 | 1 | *d* |
| 16 | 4231·4 | 23626 | 890 | 2 | *e* |
| 17 | 4246·4 | 23543 | 605 | 2 | *h* |
| 18 | 4303·9 | 23228 | 290 | 1 | *h* |
| 19 | 4311·6 | 23187 | 249 | 2 | *h* |
| 20 | 4321·9 | 23132 | 194 | 1 | *h* |
| 21 | 4396·5 | 22739 | 199 | 3 | *h* |
| 22 | 4407·3 | 22683 | 255 | 6 | *h* |
| 23 | 4415·9 | 22639 | 299 | 2 | *h* |
| 24 | 4428·7 | 22574 | 364 | 0 | *h* |
| 25 | 4460·3 | 22414 | 524 | 3 | *h* |
| 26 | 4475·0 | 22340 | 598 | 8 | *h* |
| 27 | 4496·6 | 22234 | 704 | 3 | *h* |
| 28 | 4528·6 | 22076 | 862 | 0 | *h* |
| 29 | 4534·0 | 22049 | 889 | 10 | *h* |
| 30 | 4538·2 | 22029 | 909 | 2 | *h* |
| 31 | 4544·6 | 21998 | 940 | 0 | *h* |

R. lines=$1\overline{24}(2)$, $1\overline{99}(3)$, $2\overline{54}(6)$, 287(2), $2\overline{98}(2)$, 364(0), 524(3), $5\overline{97}(8)$, 706(3), 862(0), $8\overline{89}(10)$, 909(2), 940(0).

TABLE II.

(*Raman Frequencies in cm.*$^{-1}$) $H_2SeO_3$ (*Aqueous and Alcoholic Solutions.*)

| Solid 30° C. | Molten 70° C | Aqueous solutions | | | | | Solution in MeOH | | Aq. Soln. (Pringsheim and Vost). |
|---|---|---|---|---|---|---|---|---|---|
| | | 60 % | 40 % | 30 % | 15 % | 7·5 % | 40 % | 15 % | |
| 124(1) | | | | | | | | | |
| 199(3) | | | | | | | | | |
| 254(6) | 238(1) | | | | | | | | |
| 287(1) | | | | | | | | | |
| 299(2) | 343(4) | 355(2) diff. | 355(2) | 355(1) | 355(1) | .. | | | |
| 364(0) | 380(3) | | | | | | | | |
| 524(3) | | | | | | | | | |
| | 545(1) broad | 528(0) | 528(0) | 528(0) | 528(0) | .. | | | |
| 597(8) | .. | .. | .. | .. | .. | .. | 589(*m*) (*br*) | 589(*m*) (*br*) | .. |
| 706(3) | 690(10) ± 30 | 695(6) ± 25 | 695(6) ± 25 | 695(6) ± 25 | 695(6) ± 20 | 695(6) ± 20 | .. | .. | 695 |
| 862(0) | | | | | | | | | |
| 889(10) | 892(10) ± 50 (Max. at 862) | 895(6) ± 30 | 900(6) ± 25 | 906(6) ± 20 | 906(6) ± 15 | 910(6) | 930(*m*) | 935(*m*) | 885 |
| 909(2) | | | | | | | | | |
| 940(0) | | | | | | | | | |

TABLE III.

*Raman Frequencies of Sodium Salts. Exciting line* 4358·3 A.U.

| Substance | Raman lines | | $\Delta\nu$ in cm.$^{-1}$ | Intensity | Previous work |
|---|---|---|---|---|---|
| | Wave-length A.U. | Wave-number | | | |
| $NaHSeO_3$ 15 % Aq. Solution | 4423·0 | 22603 | 335 | 1 (diff.) | 339 |
| | 4476·0 | 22335 | 603 | 1 (diff.) | .. |
| | 4527·5 | 22076 | 862 | 5 | 853 |
| $Na_2SeO_3$ 10% Aq. Solution | 4430·8 | 22563 | 375 | 1 (diff) | |
| | 4475·0 | 22340 | 598 | 0 (?) | |
| | 4502·5 | 22204 | 734 | 1 (*sh*) | nil |
| | 4517·1 | 22132 | 806 | 5 | |
| | 4527·5 | 22076 | 862 | 5 | |

### 3. *Discussion of Results.*

The crystalline acid has yielded a spectrum which is very rich in lines, all of which are sharp and well defined. These lines may be divided into five groups, namely, (1) 889 and three companions at 860, 909 and 940, (2) 706, (3) 597 and its companion at 524, (4) 287, 299 and 364 and (5) 124, 199 and 254. Of these lines, the five low frequencies as well as the strong lines 597 and 889 have yielded their antistokes. On melting the solid, all the lines of the first group merge together into one strong broad band with its centre at 892. It is definitely asymmetrical in structure and its maximum intensity is at 862.* The centre of this band shifts to a longer wave-length as the concentration of the solution falls off. Its breadth also gradually diminishes. In the alcoholic solution the shift is distinctly greater than in the aqueous solution of the same concentration by about 30 wave-numbers.

The most remarkable change takes place in the relative intensities of the second and the third group of lines. While in the solid the line at 706 is only of *medium intensity*, in the molten liquid as well as in the aqueous solutions of all concentrations it is the *strongest line* in the spectrum. Its frequency shift is also smaller by about 10 wave-numbers. This line does not at all appear in the alcoholic solutions. On the other hand, the strong line 597 of the solid appears as a faint line at 545 with a finite width in the molten state. The faint satellite 524 of this line is also probably merged into the 545 line of the solution. In the alcoholic solutions, it is the most intense line in the spectrum ; but undergoes a distinct lowering of frequency by about 8 wave-numbers.

The fourth group of lines, namely 287, 299 and 364, appear as a doublet with frequency shifts of 343 and 380 in the molten state and a single diffuse band with the centre at 355 in the aqueous solutions. Its presence could not be detected in alcoholic solutions due perhaps to the strong halation following the Rayleigh line.

Of the lines in the fifth group in the solid 124 and 199 completely disappear in the liquid and the solutions, while 254 appears but weakly only in the molten state.

Besides these lines, the water band is present in the aqueous solutions and is prominent when they are dilute. The triple structure of the band is clearly seen and no apparent change in the relative intensities of components is observed. The acid has also practically no influence on the lines of methyl alcohol.

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* A study of the polarisation of the acid shows that this line is composed by two different lines and will be reported upon in due course.

### 4. *Dissociation of Selenious Acid.*

The molecular conductivity of dilute aqueous solutions of Selenious acid[3] has been determined by Ostwald who finds that even at a dilution of 1024 litres the conductivity is only about 60% of that of a monobasic acid showing thereby, that it is a very weak acid. He has concluded that it is practically a monobasic acid which assumes the formula $(HO.SeO_2).H$. Therefore, in the aqueous solutions of all concentrations that are investigated by us, we can expect the presence of only the undissociated $H_2SeO_3$ molecules and $HSeO_3'$ ions formed during the first stage of ionisation.

The Raman specrta of aqueous solutions of concentrations varying from 100% to 7·5% by weight are identical and consist of two prominent lines at about 895 and 695 and a weak, diffuse band at 355. There is sensibly no variation also in the relative intensities of these three lines. These facts point out that the proportion of the molecular species giving rise to them remains practically the same at all concentrations.

Of these three lines, it is significant that the line 895 appears more or less in the same position in the solid, and aqueous and alcoholic solutions. Small changes in the frequency shift of this line depending upon the solvent and the state of dilution are only of an order which could be attributed to the influence of the solvent molecules. For purposes of comparison the frequency shifts of the acid and the salts are collected together in Table IV. The line which corresponds to the symmetrical expansion and contraction of $HSeO_3'$ ion appears at 862 in sodium biselenite.

The proximity of the frequency shift 895 in the acid to the symmetrical line in the biselenite suggests that the former is to be attributed to the $HSeO_3'$ ions in the acid.

On the other hand, the second intense line, 690 in the aqueous solution does not appear in the alcoholic solution, and is rendered weak in the solid; instead, another line is present at about 598 in the latter cases. These two lines presumably belong to two different forms of the undissociated molecule and are discussed fully in a later section.

The spectrum of sodium selenite consists of two lines of medium intensity with frequency shifts of 806 and 862 and two other feeble lines, as is to be expected if we assume a pyramidal model for the $SeO_3$ radical. The absence of any line at 806 at a concentration of 7·5% clearly indicates that the second stage of ionisation does not begin even at this stage.

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[3] Landolt and Börnstein Tabellen. 1112.

TABLE IV.

| $NaHSeO_3$ | $Na_2SeO_3$ | $H_2SeO_3$ (molten) | $H_2SeO_4$ 10% Aq. |
|---|---|---|---|
| | | 238 (1) | |
| 335 (1 dif.) | | 343 (4) | 327 (3 *br*) |
| | 375 (1) | 380 (3) | 390 (3 *br*) |
| 603 (1) | 598 (0) | 545 (1) | |
| | 734 (1) | 690 (10 *br*) | 737 (3 *br*) |
| | 806 (5) | | 846 (1) |
| 862 (5) | 862 (5) | | 866 (10) |
| | | 892 (10 *br*) | 910 (0) |
| | | | 929 (1) |

TABLE V.

| $NaHSO_3$ | $Na_2SO_3$ | $H_2SO_3$ | $H_2SO_4$ (incomplete) |
|---|---|---|---|
| 242 (1) | | | |
| 320 (1) | | | |
| 420 (1) | 471 (1) | | 521 |
| 565 (3) | 602 (1) | 569 | 574 |
| 826 (1) | | | |
| 985 (2) | 984 (4) | | 985 |
| 1009 (2) | | 1047 | 1047 |
| | | 1142 (*str*) | |
| | | 1199 | |

The general conclusion, therefore, regarding ionisation of the acid is that the dissociation of $H_2SeO_3 \rightarrow H^\circ + HSeO_3'$ starts from the solid and the degree of dissociation remains practically constant at the concentrations

employed. In agreement with the conductivity measurements, no further ionisation of $HSeO_3'$ is evident even in dilute solutions.

It has been reported recently that selenic acid[4] behaves in the Raman effect in the same manner as its analogue, sulphuric acid. But the selenious acid shows marked differences from sulphurous acid. In Table V the Raman frequencies of sulphurous acid and its salts are reproduced from a paper by Fadda.[5] Unlike selenious acid, there is no common likeness between the spectrum of this acid and those of Sodium sulphite and bisulphite. The lines 569 and 1047 are similar to those attributed to $HSO_4'$ ions in sulphuric acid and are, therefore, due to the oxidation of a part of sulphurous acid to sulphuric acid. As can be seen from Table V there is no such common lines between selenic and selenious acids and hence shows that the latter does not undergo oxidation so easily as sulphurous acid. The presence of the strong line at 1142 in sulphurous acid which is characteristic of $SO_2$ gas,[6] confirms that further, most of the gas exists in a state of solution with water and only a small percentage of it is probably present as $H_2SO_3$ molecules. The line 1199 has been assigned to $HSO_3'$ ions. Thus selenions acid seems to be more stable than its analogue sulphurous acid.

*5. Constitution of Selenious Acid.*

According to chemical evidence, the two possible forms in which selenious acid could exist are the symmetrical form $O = Se(OH)_2$ or the unsymmetrical form $O_2Se(OH)H$. In the former, selenium is quadrivalent and both the hydrogen atoms belong to the hydroxyl groups. In the latter, selenium is hexavalent and the acid is the pseudo-acid in which changes in constitution take place to restore it to the first type before any physical or chemical reaction starts with it. From a study of the heat of solution of this acid in different solvents Karve[7] concludes that it is an associated pseudo-acid in the pure condition and the aqueous solution contains a small percentage of the hydrate of the true acid. However, measurements of conductivity, hydrogen ion concentration, heat of solution and other physico-chemical properties do not always lead to conclusive results[8] regarding the true nature of the acid.

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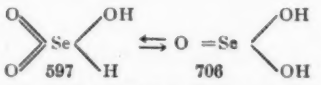
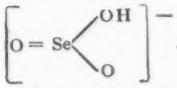
4 Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, A, 1936, **3**, 307.
5 Fadda, *Nuovo Cimento*, 1932, **9**, 168.
6 Bhagavantam, S., *Ind. Jour. Phys.*, 1931, **6**, 319.
7 Karve, D. D., *Jour. Ind. Chem. Soc.*, 1925, **2**, 128.
8 Stewart, A. W., *Some Physico-Chemical Themes*, Longmans, 1922.

From the point of view of the Raman effect it is evident that the two forms of the acid given above should yield their own lines of entirely different frequencies. As has been pointed out before, one of the striking features in the spectra of the acid in the different states of existence is the remarkable change in the intensity of the two lines 706 and 597 of the solid as it passes to solution in water. These changes in intensity could be easily understood on the postulate that the two forms of the acid are in a state of dynamic equilibrium as follows :—




The line with a frequency shift of 597 is characteristic of the unsymmetrical type and 706 of the symmetrical type. The former is more predominant than the latter in the solid and hence the increased intensity of the line 597. The existence of the line 706, in the crystalline acid shows that the latter type is also present in it. As is to be expected, solution of the acid in methyl alcohol contains only the unsymmetrical form and gives the intense line at about 589. In the aqueous solution the reverse process sets in and almost the whole of the acid assumes the symmetrical structure. This contributes to the increased intensity of the line 706. In the molten state when the acid is in solution with its water of crystallisation, a weak line is present at 567 and indicates the persistence of the unsymmetrical form under that condition.

According to the theory of pseudo-acids the first ionisation product of both the types of molecules is identical and the biselenite ion has a structure 

. Hence irrespective of the molecular species existing in the solid and the aqueous and the alcoholic solutions, a certain percentage of $HSeO_3'$ ions is formed during the first stage of dissociation and this accounts for the appearance of the line of frequency shift of 895 more or less in the same position in all states.

Thus, the solid or the soultions present a complicated system consisting of two or three molecular species and it is difficult to assign the low frequencies that are observed to any one of them. But in comparison with the Raman spectra of iodic acid[9] or nitric acid, it may be suggested that the two low frequencies at 343 and 380 in the molten liquid which appear as a single diffuse line at 355 in more dilute solutions

[9] Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, A, 1935, 2, 119.

belong to the vibrations corresponding to the second parallel vibration of the molecules of the $AX_3$ type. Of these 343 coincides fairly well with the low frequency at 335 in the sodium biselenite and is due to $HSeO_3'$ ions. The corresponding line of the $SeO_3$ radical appears at 375 in the sodium selenite solution. The other frequency 380 may, therefore, belong to the symmetrical form of $H_2SeO_3$ molecules. As has been discussed before, these two frequencies of the solution are replaced by three sharp lines 287, 299 and 364 in the solid. There is one more line at about 524 which is of medium intensity in the solid and which is present weakly in the aqueous solutions of the acid. This line is also to be attributed to one of the normal modes of vibration of the $H_2SeO_3$ molecule. The corresponding line of $HSeO_3'$ ion appears diffuse at 603 in the biselenite and of $SeO_3$ radical appears at 734 in the selenite of sodium.

### 6. *Low Frequency Oscillations.*

Besides the lines discussed above, there are three lines at 124, 199 and 254 in the solid. Their antistokes are clearly seen in the excitations by the 4047 radiations of the mercury arc. The first two completely vanish on going to solution and the third appears weakly only in the molten state. In the case of iodic acid and iodates,[10] the author has observed similar lines and pointed out some difficulties in assigning them to lattice oscillations as put forward by Gross and Vuks[11] to explain the lines discovered by them in the crystals of diphenyl ether, naphthalene, dibromobenzene and benzene. Bhagavantam[12] has suggested that in the latter cases the lines are due to the incomplete rotations of molecules as pictured by Pauling. Recently Sirkar[13] has investigated the problem more thoroughly and finds that these lines owe their origin to intermolecular vibrations in groups of molecules which persist in some cases in solution and that they are affected by changes of temperature. In view of these discussions, it is probable that the line 254 of the crystals of selenious acid which appears feebly in the liquid state is due to polymerised groups of molecules and the lines 124 and 199 are due to hindered rotation of individual molecules. But a more definite conclusion can be arrived at only by studying the effect of change of temperature on these lines and work in this direction is in progress.

### 7. *Change of State and Raman Effect.*

The changes that take place in the main Raman lines of selenious acid as it passes from the solid to the molten state are illustrated in the accompanying

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[10] Venkateswaran, C. S., *loc. cit.*

[11] Gross and Vuks, *Nature*, 1935, **135**, 100, 431, 998; *Jour. de Phys.*, 1935, **6**, 457.

[12] Bhagavantam, S., *Proc. Ind. Acad. Sci.*, A, 1935, **2**, 63.

[13] Sirkar, S. C., *Ind. Jour. Phys.*, 1936, **10**, 109.

plate. Just as in the case of selenic acid[14] the sharp lines of the solid are replaced by broad and intense bands which tend to become narrower in the less concentrated solutions. The extraordinary breadth of these bands is partly explained by supposing that they consist of several components which appear as single, sharp lines in the crystals. But, in general, this feature is characteristic of associated liquids like sulphuric, iodic, formic and acetic acids and therefore, is to be attributed to association of molecules in them. In nitric acid in which there is no association the lines are comparatively sharp. The lines also suffer changes in frequency which is characteristic of hetro-polar compounds. In both selenic and selenious acids this change is pronounced in the lower degenerate vibrations.

In conclusion, the author wishes to thank Professor Sir C. V. Raman for his keen interest in the work.

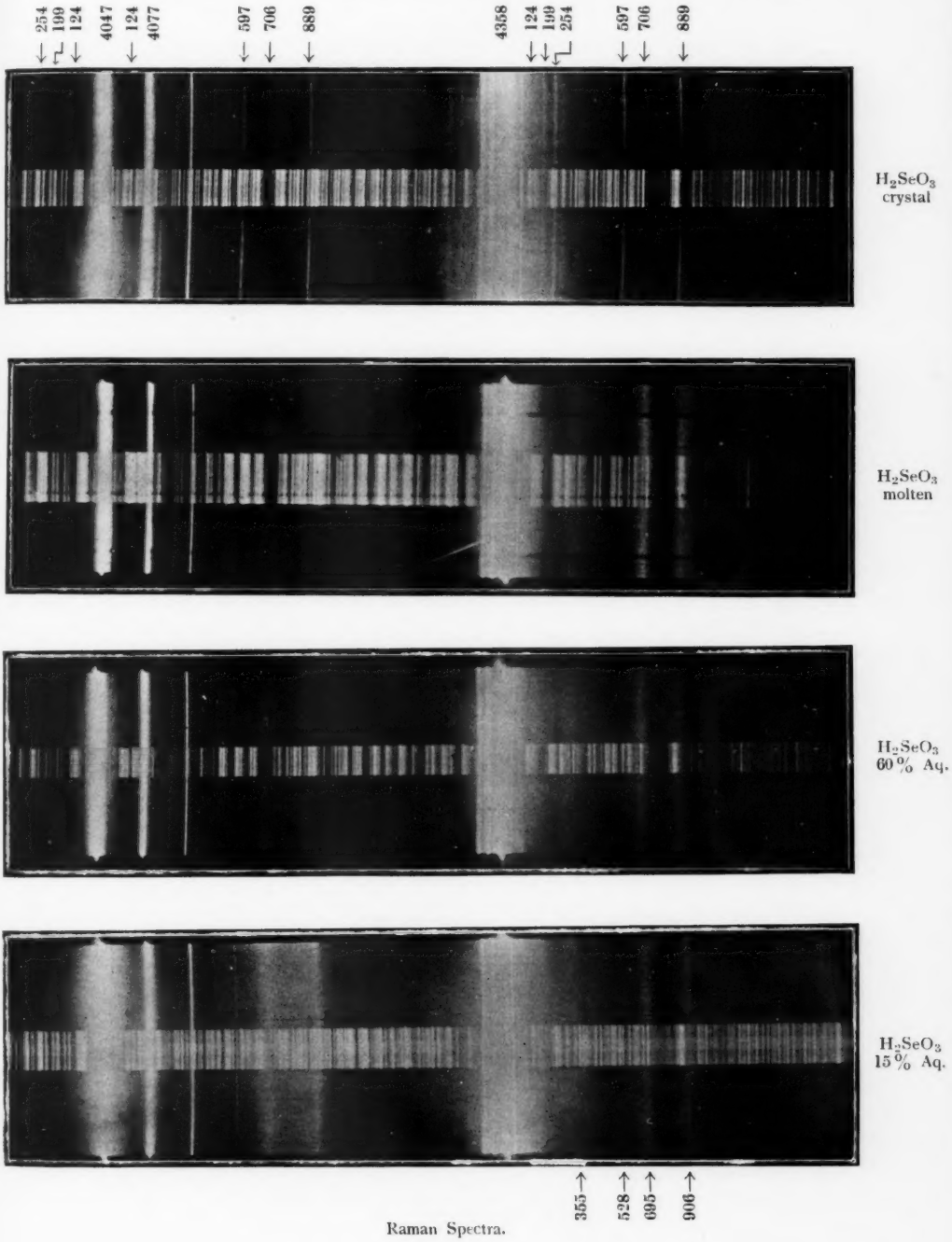
*Summary.*

The Raman spectra of selenious acid as crystals and as aqueous and alcoholic solutions of varying concentrations as well as those sodium biselenite and sodium selenite are investigated. The solid has yielded a spectrum rich in sharp and intense lines, of the following frequencies :—124, 199, 254, 287, 299, 364, 524, 597, 706, 862, 889, 909 and 940 cm.$^{-1}$ The lines broaden out and undergo variations both in frequency shift and intensity.

The changes in relative intensities of the two lines, 706 and 597, are particularly remarkable and are explained by postulating two types of molecules namely the symmetrical form $O = Se(OH)_2$ and the unsymmetrical form $O_2Se(OH)H$ in dynamic equilibrium in the acid. In the solid and in the solution in methyl alcohol the latter is the more predominent type and in the aqueous solution almost the whole of the acid is converted to the former type. Thus the Raman effect data are made use of for the first time to explain the pseudo or the true nature of the acid.

The spectra of aqueous solutions of different concentrations indicate that the dissociation of the acid is weak and that, the proportion of molecules dissociated to $HSeO_3'$ ions remains practically constant throughout. The line 895 is assigned to the $HSeO_3'$ ions. The results are compared to those of its analogue, sulphurous acid. The other lines in the spectrum are attributed to vibrations of definite molecular species by comparing them to the lines in the sodium salts of the acid.

[14] Venkateswaran, C. S., *loc cit.*




Raman Spectra.

Three low frequencies of the solid at 124, 199 and 256 are discussed in the light of the existing theories and their probable assignment is indicated.

The influence of change of state of the Raman spectra of the acid is briefly discussed. The broadening of the lines in the liquid is explained as due partly to association in the molecules and partly to the composite nature of the bands.

# RESONANCE CURVES FOR A QUARTZ OSCILLATOR IMMERSED IN LIQUIDS.

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## *Introduction.*

It is well known that resonance for a quartz crystal in air is sharp and is always found not of a symmetrical shape, but steeper towards the higher frequency side. A little broadening on the side of the lower frequency has been explained on the basis that the resistance of the oscillatory circuit changes slightly on tuning to lower frequency for the same circuit, and that such increase in resistance for high frequency current, though small, does affect its shape. Such an effect can be easily demonstrated by the addition of more resistance to the circuit when the resonance curve itself is found to get flatter and less in height. So much so, when the resonance curve is so markedly changed by internal resistance, it was thought that a similar resistance added to the quartz crystal, having the effect of damping its oscillations, might also produce similar or allied changes in the form of the resonance curves. This paper gives results of such experiments carried out with some organic liquids, and the effect of the damping by such liquids on the frequency of the oscillator. Work was also carried out on the relationship between the resonance curve and the diffraction spectra obtained at frequencies, at resonance and near about it.

### *A. Diffraction Spectra at Resonance and Near about It.*

A series of photographs of the diffraction of light by the ultrasonic waves in *o*-xylene (Table VI ; Fig. 1) were taken at the resonance frequency of the quartz crystal and at frequencies on either side of it. The radio-frequency current was measured by means of a r.f. milliammeter while the photographs were taken just at those frequencies. Fig. 1 gives these spectra for 5461 Å with the frequencies and the current marked on either side of each spectrum. It is seen that for maximum current in the oscillatory circuit, *i.e.*, $I_r = 490$ mA, when the crystal vibrates at the point of resonance, the frequency is given by $7 \cdot 33 \times 10^6$ c./s. Thereafter the current diminishes while the frequency also continues to diminish.

With regard to the diffraction spectra, we should naturally expect the number of orders to be a maximum for maximum oscillatory current. But this is found not to be the case. On tuning from a frequency higher than the resonance, it is observed that while the current slowly increases the number of diffraction orders making their appearances also slowly increases. At the resonance frequency of $7 \cdot 33 \times 10^6$ c./s. the number of orders is 3 with a faint fourth. On still further decreasing the frequency the current also decreases, but not so the number and intensity of the diffraction spectra. The maximum number of orders, of 6, occurs at $7 \cdot 17 \times 10^6$ c./s. and for an oscillatory current of only 350 m.a. much less than what it was at the resonance. Visually it was clearly noticed that from the point of resonance to another of lower frequency, the intensity of diffraction spectra increased, and then for still lower frequencies of oscillation, the number and intensity both decreased continuously. In other words, the maximum number of diffraction orders does not coincide with maximum oscillatory current, and it was so, not alone with *o*-xylene for which the photograph is reproduced but for all liquids examined so far. It seems strange that this phenomenon should occur only on one side of the resonance frquency, *i.e.*, always on the side of lower frequency.

### *B. Resonance Curves in Liquids.*

Having found some anomalies regarding the relationship between the oscillatory current and the number of diffraction orders, it became necessary to analyse it completely. Towards that end, resonance curves for the quartz in some typical liquids were taken, liquids of varying viscosity.

In order to get accurately such curves it is necessary that error in the r.f. current should not creep in anywhere to make the results anomalous. The oscillatory current, for any particular frequency, will change, if the anode potential, the filament current or the grid bias should change even by ever so little. Hence precautions to keep these steady and constant were taken at every stage, and for every liquid studied.

The liquids experimented on were benzene, carbon-tetrachloride, carbon-disulphide, anisol, cyclohexanone and glycerine, of which the last member possesses greatest viscosity in the above series, following closely cyclohexanone.

For different points in tuning, the frequencies were determined accurately by a Precision wave-meter, while the oscillatory currents were indicated by a Weston radiofrequency milliammeter of the thermocouple type. Other readings of H.T. voltage, d.c. current were noted to check up the accuracy, from liquid to liquid.

TABLE I. *Benzene*

| Frequency in megacycles per second | Current in the Oscillatory circuit in $m$ A = I | $\frac{I^2}{I_r^2}$ |
|---|---|---|
| 7·51 | 110 | ·050 |
| 7·493 | 175 | ·128 |
| 7·47 | 260 | ·282 |
| 7·46 | 330 | ·454 |
| 7·44 | 400 | ·666 |
| 7·43 | 445 | ·825 |
| 7·41 | 490 = $I_r$ | 1·000 |
| 7·335 | 445 | ·825 |
| 7·275 | 390 | ·634 |
| 7·18 | 350 | ·511 |
| 7·07 | 310 | ·400 |
| 7·00 | 260 | ·282 |
| 6·94 | 200 | ·167 |

TABLE II. $CCl_4$

| Frequency in megacycles per second | Current in the Oscillatory circuit in $m$ A = I | $\frac{I^2}{I_r^2}$ |
|---|---|---|
| 7·53 | 100 | ·042 |
| 7·50 | 150 | ·094 |
| 7·48 | 290 | ·350 |
| 7·46 | 345 | ·496 |
| 7·448 | 395 | ·650 |
| 7·41 | 490 = $I_r$ | 1·000 |
| 7·35 | 455 | ·862 |
| 7·265 | 400 | ·666 |
| 7·13 | 335 | ·467 |
| 7·03 | 300 | ·375 |
| 6·96 | 230 | ·220 |

TABLE III. *Carbon-disulphide*

| Frequency in megacycles per second | Current in the Oscillatory circuit in $m$ A = I | $\frac{I^2}{I_r^2}$ |
|---|---|---|
| 7·53 | 100 | ·061 |
| 7·50 | 210 | ·269 |
| 7·48 | 260 | ·412 |
| 7·46 | 290 | ·513 |
| 7·448 | 355 | ·768 |
| 7·41 | 405 = $I_r$ | 1·000 |
| 7·335 | 375 | ·857 |
| 7·255 | 335 | ·684 |
| 7·13 | 295 | ·530 |
| 7·052 | 250 | ·381 |
| 6·98 | 205 | ·256 |
| 6·92 | 150 | ·137 |
| 6·89 | 130 | ·103 |

TABLE IV. *Anisol*

| Frequency in megacycles per second | Current in the Oscillatory circuit in $m$ A = I | $\frac{I^2}{I_r^2}$ |
|---|---|---|
| 7·55 | 100 | ·058 |
| 7·51 | 130 | ·098 |
| 7·48 | 250 | ·363 |
| 7·45 | 340 | ·671 |
| 7·42 | 405 | ·953 |
| 7·41 | 415 = $I_r$ | 1·000 |
| 7·335 | 390 | ·884 |
| 7·255 | 350 | ·712 |
| 7·10 | 310 | ·558 |
| 6·98 | 250 | ·363 |
| 6·92 | 210 | ·256 |
| 6·852 | 160 | ·149 |
| 6·78 | 110 | ·070 |

TABLE V.
*Cyclohexanone*

| Frequency in megacycles per second | Current in the Oscillatory circuit in $m$ A = I | $\frac{I^2}{I_r^2}$ |
|---|---|---|
| No reading obtainable | 220, 230, etc. | |
| 7·598 | 250 | ·743 |
| 7·51 | 260 | ·804 |
| 7·480 | 265 | ·835 |
| 7·41 | 290 = $I_r$ | 1·000 |
| 7·10 | 250 | ·743 |
| 7·012 | 210 | ·524 |
| 6·948 | 180 | ·385 |
| 6·91 | 150 | ·268 |
| 6·812 | 110 | ·144 |
| 6·78 | 100 | ·119 |

TABLE VI.
*In o-xylene (in Plate* XXVII)

| No. | Frequency in megacycles per second | Current in the Oscillatory circuit in $m$ A = I | $\frac{I^2}{I_r^2}$ |
|---|---|---|---|
| 1 | 7·50 | 180 | ·135 |
| 2 | 7·478 | 260 | ·282 |
| 3 | 7·45 | 350 | ·510 |
| 4 | 7·41 | 450 | ·843 |
| 5 | 7·33 | 490 = $I_r$ | 1·000 |
| 6 | 7·25 | 420 | ·735 |
| 7 | 7·17 | 350 | ·510 |
| 8 | 7·04 | 290 | ·350 |
| 9 | 6·93 | 215 | ·193 |
| 10 | 6·873 | 150 | ·094 |

(For a second quartz crystal)

Tables I to V give the relavent readings of frequencies, with radio-frequency current, in different liquids. To get actually the curves for these liquids in a form for comparison, it is better to take the ratio $\left(\frac{I^2}{I_r^2}\right)$; of the square current at any frequency ( $= I^2$) to the square of the current at the resonance frequency ( $= I_r^2$) ; which ratio will be given at the resonance by a value = 1 for all liquids. Then the curves will be uniform and superposable.

Such curves for the liquids investigated are given in Fig. 2.

The curves are always much steeper towards the higher feequency, while they spread out on the side of the lower frequency. This is characteristic of all liquids, and indeed so in air also. This is usually explained on the basis that the resistance of the oscillatory circuit is not the same for all frequencies, and that it is higher for lower frequencies. This offers a natural explanation as to why the resonance curves in lquids should be much more spread on the side of lower frequencies. We shall examine the resonance curves for these liquids, each part separately.

*Higher frequency range.*—The curves for benzene, carbon-tetrachloride, carbon-disulphide and anisol are almost steep, but quite distinct with very little separation between each. That for cyclohexanone starts very much

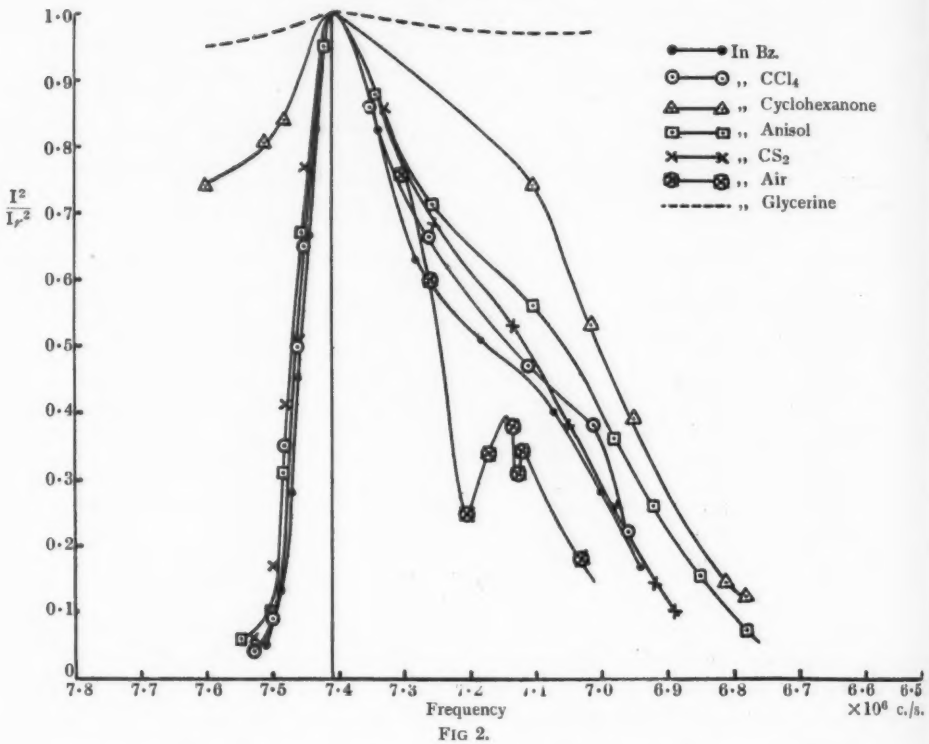


FIG 2.

higher, at $\frac{I^2}{I_r^2} = 0 \cdot 8$ for a frequency for which the liquids above mentioned have $\frac{I^2}{I_r^2}$ equal to 0·05. For glycerine the corresponding value for $\frac{I^2}{I_r^2} = 0 \cdot 95$.

*Lower frequency range.*—The curves for each liquid have now become distinct and separate from each other. That for benzene falls rather rapidly while glycerine maintains its top level. Cyclohexanone takes a path midway between these two, while the curves for other liquids fall below that for cyclohexanone. One remarkable feature on this portion of the resonance curves is that, those lines which were crowded on the side of the higher frequency, namely those for benzene, carbon-tetrachloride, carbon-disulphide and anisol, are here clearly resolved and separated.

If we now compare the viscosities for these liquids, with say, the ratio of $\frac{I^2}{I_r^2}$ for a frequency $7 \cdot 20 \times 10^6$ c./s. at which point they are all resolved, we find these curves, surprisingly enough to follow the same order as that for viscosities. Benzene with lowest viscosity (except $CS_2$) has a high

gradient, while glycerine shows almost no gradient, it possessing the highest viscosity in this series. All liquids follow this order. Here it may be remarked that for some reason yet unknown carbon-disulphide behaves anomalously.

TABLE VII.

*Viscosity and Damping.*

| No. | Liquids | Viscosity at 25°C. (from I. C. T.) | $\frac{I^2}{I_r^2}$ at $7 \cdot 20 \times 10^6$ c./s. (from fig. 2) | Oscillatory current in *m* A (shown in fig. 2) |
|---|---|---|---|---|
| 1 | Benzene .. | 0·00604 | 0·53 | 490 |
| 2 | Carbon-tetrachloride .. | 0·008876 | 0·57 | 490 |
| 3 | Carbon-disulphide .. | 0·00356 | 0·61 | 405 |
| 4 | Anisol .. | 0·0101 | 0·65 | 415 |
| 5 | Cyclohexanone .. | 0·028 | 0·86 | 290 |
| 6 | Glycerine .. | 8·2 | 0·98 | $<30$ |

These facts are brought forward separately in Table VII and the agreement between the observed order of resolution of these curves and the order of viscosity is good. It is very clear now that the lower frequency portion of the resonance curve is very deeply connected with the nature of the liquid, more especially its viscosity, and work, of the nature of, diffraction of light by ultrasonic waves, carried out in that part of the curve will, it is hoped, give more information regarding the nature of the liquid and the effect of damping.

### *C. Effect of Damping.*

It is pertinent to enquire at this stage whether any effect due to damping was observed or not. There are two distinct effects to be expected from damping: (*a*) a shift in the frequency and (*b*) a lowering of the amplitude of vibration, and directly here, lowering of the supersonic intensity. In the audible range, effect due to (*a*) is negligible and ordinarily it is not noticed while (*b*) under certain conditions can be detected. Ultrasonic range is especially suited for noticing both the effects under (*a*) and (*b*).

*Case* (*a*) :—The experimental arrangement required a slight modification of the technique. The quartz crystal was as usual suspended between two metal contacts and held in a particular position without disturbance. Having obtained a certain frequency of vibration, the entire apparatus was

left undisturbed, without even touching any part. The tall vessel containing the liquid was slowly raised from just underneath the crystal, till one side of the quartz piece was well under the liquid. The crystal as a whole was not immersed. Now the crystal was set into vibration, with current and voltage properly adjusted ; and the electrical wave-length was carefully measured by means of a Precision wave-meter. The trough was lowered and the liquid removed for experimenting with another liquid. The quartz piece was carefully washed, *in situ*, with volatile solvents, without in any way disturbing the arrangement. Readings for frequencies, with quartz in other liquids, were taken in the same way. To see that it was not in any way disturbed, the frequency of oscillation of the quartz in air was taken every time, before and after each experiment, and it was faithfully reproduced every time, being the same as the one in the very beginning. Hence it was concluded that no external disturbance could have affected the frequency, and any change observed was due to the damping effect in the liquid and to it alone.

The frequency of vibration was taken first in air ; and then in the following liquids : benzene ; toluene ; *o*-, *m*- and *p*-xylenes ; carbon-tetrachloride ; carbon-disulphide ; anisol ; and cyclohexanone. Table VIII gives the frequencies as obtained in this set of experiments.

TABLE VIII.

*Shift in Frequency due to Damping.*

| No. | Liquids | Frequency in megacycles per second (measured by wave-meter) | Damping co-efficient (standard = air) |
|---|---|---|---|
| 1 | Benzene .. | 7·285 | $0·715 \times 10^6$ |
| 2 | Toluene .. | 7·285 | ,, |
| 3 | *o*-xylene .. | 7·285 | ,, |
| 4 | *m*-xylene .. | 7·285 | ,, |
| 5 | *p*-xylene .. | 7·285 | ,, |
| 6 | Carbon-tetrachloride .. | 7·280 | $0·764 \times 10^6$ |
| 7 | Carbon-disulphide .. | 7·280 | ,, |
| 8 | Anisol .. | 7·280 | ,, |
| 9 | Cyclohexanone .. | 7·262 | $0·920 \times 10^6$ |
| 10 | In air .. | 7·320 | Standard |

It is well known that if we know the two frequencies, with and without damping, $k$ the co-efficient of damping can be easily calculated from the

formula

$$n' = \sqrt{n^2 - k^2}$$

where $n'$ is the damped frequency and $n$ the natural frequency. Column 3 in the table gives the co-efficients of damping as calculated by this formula, with the frequency of oscillation in air as the standard.

It appears from these results that damping from air to liquids generally is considerable, as seen from the diminution in frequency from $7 \cdot 320 \times 10^6$ c./s. to $7 \cdot 285 \times 10^6$ c./s. But between liquids themselves, when there is great difference in viscosity, as between benzene and cyclohexanone or glycerine, then again there is a small diminution in the frequency. The table shows these effects very clearly.

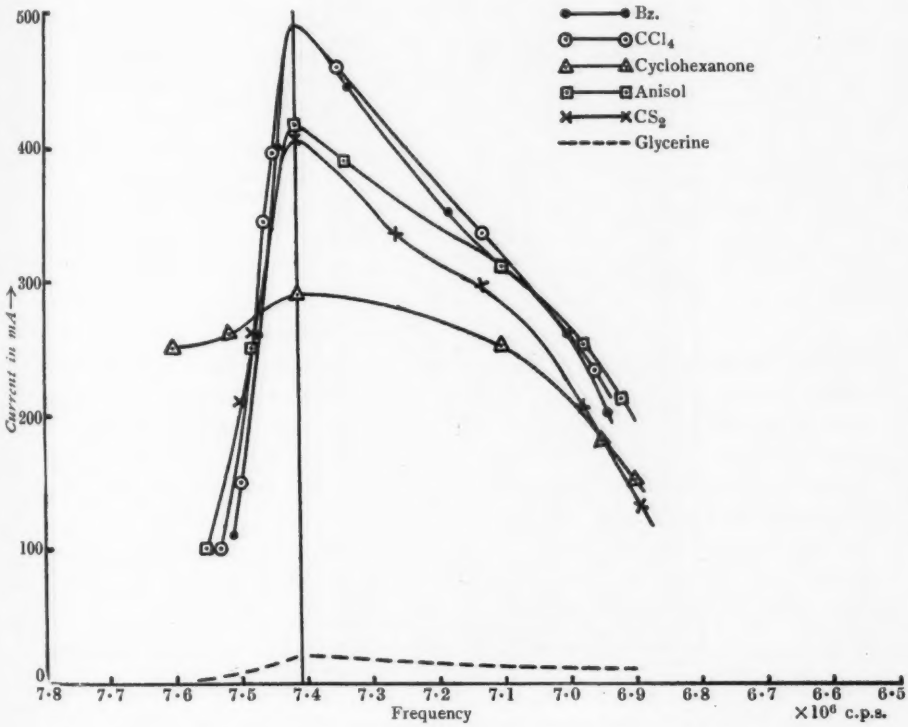


FIG. 3.

*Case* (*b*) :—Fig. 3 gives the relation between frequency at resonance and near about it, and the oscillatory current. The damping, as measured by the current is also indicative of the diminution in supersonic amplitude. The

current is less for more highly viscous liquids, such as cyclohexanone and glycerine, and the curves are also more flat. Tables I to V give the results.

The conditions are true if the quartz crystal has one face immersed in the liquid. It was thought desirable to see whether the damping increased with depth, to which depth the crystal was immersed, for then we know that the effective damping is increased at greater depths. The following table (Table IX) gives the relation between the depth, the frequency and the damping co-efficient. It is clear that damping increases with depth, as is to be expected.

TABLE IX.

*Effect of Depth on Damping : in Toluene.*

| | Depth in cms. of the Quartz crystal | Frequency in mega-cycles per second | Damping co-efficient |
|---|---|---|---|
| 1 | One surface in contact with liquid .. | 7·285 | Standard |
| 2 | Quartz just immersed .. | 7·250 | $0·714 \times 10^6$ |
| 3 | Quartz, 2 cms. below surface .. | 7·210 | $1·043 \times 10^6$ |
| 4 | Quartz, 4 cms. below surface .. | 7·160 | $1·345 \times 10^6$ |

*D. Range and Sharpness of Resonance.*

It is known from the work of Barton and others, that there are two features to be distinguished in any resonance curve, namely, (1) the range and (2) the sharpness. The curve is sharper for less damping, while the range becomes less at the same time. Also, the curve is much sharper at higher frequencies than for lower, when the liquid used for damping the vibrations is the same.

Fig. 2 gives the resonances in a number of liquids of varying damping co-efficients. It is seen from the curves that for liquids of greater viscosity—and therefore greater damping—the range is greater and not sharp at all. This is seen to be so for glycerine and cyclohexane. The range for the same amplitude $\frac{I^2}{I_r^2} = 0·75$, is 7·10 to 7·58 megacycles for cyclohexane, while it is only 7·30 to 7·43 megacycles for benzene. Fig. 3 gives an idea of the flatness of the curves.

Another point of interest is to get resonance curves for different harmonics of the crystal in the same liquid—whereby damping is kept constant—and compare the range and sharpness of such curves at different frequencies.

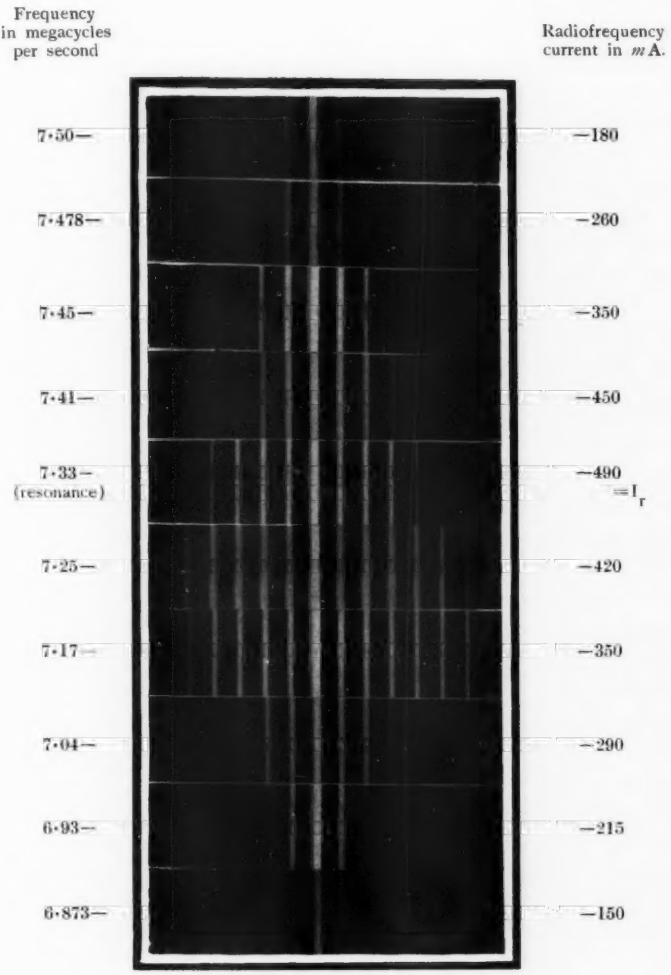


FIG. 1. Diffraction spectra in *o*-Xylene near the resonance frequency of a quartz oscillator (for 5461 Å).

Theory shows that the resonance at higher frequencies must be much sharper than at lower frequency, when the damping is constant. Benzene was chosen as the liquid for the quartz oscillator and a frequency of $20 \cdot 00 \times 10^6$ c./s. was employed as the higher harmonic. It was found that the resonance was very sharp and its range did not extend much, as it was found that even a slight disturbance was enough to make the diffraction spectra, produced by the crystal oscillating in the liquid, disappear. The oscillatory current was also taken as an indicative. This is only qualitative, as even an exact quantitative measurement will not be comparable with the one at $7 \cdot 41 \times 10^6$ c./s., since the conditions of experiment will not be identical. The resistances of the circuits, which are important factors in such resonance curves, will not at all be comparable. But, withal, a qualitative test was found to be in agreement with theory.

The general ideas developed regarding the range and sharpness of resonance curves are found to hold good in the region of ultrasonics.

The author records his grateful thanks to Prof. Sir C. V. Raman for constant interest in the work.

*Summary.*

The paper gives results of investigation with regard to the resonance curves of a quartz oscillator immersed in liquids. Each curve is characteristic of the liquid and is resolved one from another very clearly only on the lower frequency region of the curve. The order of resolution observed is the order of the viscosities of the liquids. It was also noticed that a greater number of diffraction orders was observed, not at the resonance of the crystal, but at a point of lower frequency, corresponding to the region of clear resolution of the resonance curves. The effects of damping, namely (1) a shift in frequency and (2) flatness of the resonance curve are observed and recorded. The range and sharpness of resonance have been compared (*a*) as between different liquids of different damping co-efficients at a given frequency, and (*b*) in one liquid but at different frequencies (higher harmonics). For condition (*a*) range extends while the sharpness diminishes for highly viscous liquids, while for condition under (*b*) the sharpness increases with diminished range at higher frequency.

# ROTATIONAL ANALYSIS OF THE ÅNGSTRÖM BANDS AT λλ 6080 AND 6620 Å.U.

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The Ångström bands of CO, though simple in structure, inasmuch as they are due to the transition $B^1\Sigma \rightarrow A^1\Pi$, have evoked considerable interest from more than one point of view. The rotational analysis of some of these bands was given by Hulthen.[1] The 0–0 and 1–0 bands were analysed by Jassé,[2] by Johnson and Asundi[3] and by Rosenthal and Jenkins.[4] The latter were able to show that pronounced perturbations of the rotational levels occurred in the bands they analysed, *viz.*, bands having $v'' = 0, 1, 2$ and 3, and especially in bands with $v'' = 0$ and 1, these perturbations occurred at relatively low J values in addition to perturbations at high J values observed in all bands. The displacements of the 0–1 and 1–1 bands previously observed by Johnson and Asundi was traced to this rotational perturbation very near to the origin in these cases. All these perturbations are definitely shown to be in the $A^1\Pi$ level. Further proof of this fact is given by similar perturbations observed by Read[5] in such of the fourth positive carbon bands as have initial levels of the same quantum number as the final levels of the Ångström bands. The initial state $B\ ^1\Sigma$ of these latter bands is also not without interest. Recently, Coster and Brons[6] have reported a sudden decrease in intensity of some of the rotational lines which they attribute to pre-dissociation of the molecule. The present paper deals with the rotational analysis of the 0–4 and 0–5 bands, preliminary results of which have been published before.[3] Measurements have been made on plates taken in the first order of a 21 ft. concave grating. The spectrum was produced in a usual discharge tube of CO and the data are confined to relatively low J values on account of the low temperature production of the bands.

Tables I and II contain the analysed wave-numbers (cm.$^{-1}$) *in vacuo* of the lines of the two bands. Table III contains the $\Delta_2F'(J)$ values observed in these bands and those calculated by Rosenthal and Jenkins. On account of the $\Lambda$-type doubling in the lower level, combination defects are to be expected, but these are negligible in such at least of the bands as are free from perturbations at low J values. Table IV gives the R(J) – Q(J)

and $Q(J+1) - P(J+1)$ values which should be equal if no combination defects were present, these being then $\Delta_1F'(J)$ values; also similarly the $R(J) - Q(J+1)$ and $Q(J) - P(J+1)$ values which would be $\Delta_1F''(J)$.

The agreement between the observed and calculated values of $\Delta_2F'(J)$ in Table III is quite satisfactory and affords proof of the correctness of the analysis. Reference to Table IV shows that combination defects are negligible for the 0–5 band at $\lambda$ 6620. This indicates that there are probably no perturbations in this band upto the J values here observed. In order to ascertain this, the method used by Rosenthal and Jenkins of plotting deviation curves was adopted. Formulæ were developed to express the regular lines of each branch in the bands by the method of least squares and the observed *minus* calculated values were graphically plotted. The small residuals for the band at $\lambda$ 6620 (the maximum *O–C* values being + 0·22 for P(1), + 0·20 for Q(13) and + 0·18 for R(3), indeed confirm that there are no perturbations in this band inside the observed limit. This is further corroborated by the recent work of Gerö[13] on the fourth positive carbon band ($v' = 5$, $v'' = 13$), which involves this same level. The first strong perturbation observed by Gerö at Q(30) is already outside the limit of the present observations. On the other hand, the band at $\lambda$ 6080 shows considerable combination defects and correspondingly large residuals for the P and R branches, the Q branch, however, being more or less normal. The residuals increase towards small J values starting from + 0·06 at P(6) to + 0·94 at P(2) and from + 0·06 at R(6) to + 1·04 at R(2), and therefore point to $J = 0$ being perturbed as in the 0–1 or 1–1 bands, the perturbation being smaller than and opposite in sign to that observed in the latter bands. This perturbation, though small, appears to be genuine because firstly while $\Delta_2F'(J)$ values are proper, the combination defects are appreciable and secondly, the positive residuals increase towards $J = 0$ thus indicating a violet shift of the origin which has been already noticed.[3] Incidentally, a second perturbation at P(19) is indicated by the residuals, − 0·28, − 0·52 and − 0·43 for P(18), P(19) and P(20) respectively.

Coster and Brons[12] find a perturbation in this band at about $J = 31$ for this level but Gerö[13] has shown, from a study of the Herzberg and the fourth positive carbon bands involving this level that perturbations occur at $J = 0$, 23 and 37. The present results confirm the perturbation at $J = 0$ but the data are not sufficient to confirm the other perturbations. The very small perturbation at about $J = 19$ has not been recorded previously and may not be real.

Rosenthal and Jenkins[4] have come to the conclusion that the perturbations are caused by the rotational terms of the electronic state $a\,^3\Pi$. Watson[7]

from Zeeman effect results also favours this interpretation. Coster and Brons[13] classify them as due to the already known states $a'^3\Sigma^+$ and $d^3\Pi$ and to certain $e^3\Sigma^-$ and $^1\Pi$ states which are still unknown. In view of the multiple perturbations in each band, such an explanation appears quite plausible. Except for the hypothetical $^1\Pi$ state, all perturbing levels would then, however, be triple. This creates a theoretical difficulty pointed out by them, which concerns the condition that for the two terms to perturb they must have the same symmetry with respect to interchange of the point co-ordinates of the electrons, that is, they must be terms of equal multiplicity.[8] There is, however, a possibility of explaining some of these perturbations as due to the ground $X^1\Sigma$ state of the molecule. It is of course not possible to extrapolate with much accuracy but if we do so from the equation given by Read[5] for the fourth positive carbon bands, we obtain for the vibrational terms of the ground level, values which are comparable with those of the $A^1\Pi$ state which is perturbed, as in the following table :—

| $X^1\Sigma$ Level | | $A^1\Pi$ Level | |
|---|---|---|---|
| $v$ | Energy cm.$^{-1}$ | $v$ | Energy cm.$^{-1}$ |
| | | 0 | 65809 |
| 40 | 66865 | 1 | 67297 |
| 41 | 68006 | 2 | 68739 |
| 42 | 69124 | 3 | 70151 |
| 43 | 70217 | 4 | 71527 |
| 44 | 71288 | 5 | 72869 |

If the extrapolation gave correct values, from this table one would expect that of all levels, only $v = 3$ of $A^1\Pi$ state would exhibit near $J = 0$, a perturbation due to $v = 43$ of $X^1\Sigma$ state. This, however, has no support from experimental evidence and therefore the coincidence is simply fortuitous and the extrapolation is certainly only approximate. We know, however, that $v = 1$ of $A^1\Pi$ state is perturbed near $J = 0$ and if we assume that this perturbation is caused by $v = 40$ of $X^1\Sigma$ state, it is possible that a similar perturbation near the origin at $v = 4$ of the $A^1\Pi$ state is caused by $v = 44$ of the $X^1\Sigma$ state within the errors of extrapolation. It appears as if some of the perturbations, therefore, are definitely due to the ground level of the

TABLE I.

*Analysis of* 0–4 *Band at* λ 6080 *Å.U.*

(*Figures in brackets denote estimated Intensities.*)

| J | P-Branch | Q-Branch | R-Branch |
|---|---|---|---|
| 1 | .... | 16450·48 (6) | .... |
| 2 | 16444·81 (0) | 452·37 (2) | 16464·10 (0) |
| 3 | 443·52 (6) | 454·97 (3) | 470·71 (1) |
| 4 | 443·13 (3) | 458·53 (4) | 478·13 (1) |
| 5 | 443·52 | 462·95 (4) | 486·45 (2) |
| 6 | 445·01 (5) | 468·25 (8) | 495·61 (2) |
| 7 | 447·33 (4) | 474·49 (8) | 505·67 (2) |
| 8 | 450·48 | 481·48 (8) | 516·64 (2) |
| 9 | 454·50 (4) | 489·41 (7) | 528·43 (2) |
| 10 | 459·36 (3) | 498·19 (7) | 541·09 (2) |
| 11 | 465·06 (4) | 507·84 (7) | 554·59 (2) |
| 12 | 471·73 (3) | 518·39 (7) | |
| 13 | 479·21 (3) | 529·82 (7) | |
| 14 | 487·63 (2) | 542·01 (5) | |
| 15 | 496·84 (2) | 555·21 (5) | |
| 16 | 506·95 (2) | | |
| 17 | 518·14 (1) | | |
| 18 | 529·82 | | |
| 19 | 542·55 (0) | | |
| 20 | 556·32 (0) | | |

TABLE II.

*Analysis of* 0–5 *Band at* λ 6620 *Å.U.*

(*Figures in brackets denote estimated Intensities.*)

| J | P-Branch | Q-Branch | R-Branch |
|---|---|---|---|
| 1 | 15104·24 (0) | 15108·07 (1) | 15115·62 (1) |
| 2 | 102·12 (1) | 109·93 (2) | 121·67 (0) |
| 3 | 100·89 (5) | 112·72 (5) | 128·24 (2) |
| 4 | 100·89 | 116·38 (5) | 135·86 (2) |
| 5 | 101·50 (3) | 121·00 (7) | 144·41 (4) |
| 6 | 103·17 (7) | 126·55 (8) | 153·87 (3) |
| 7 | 105·73 (5) | 132·96 (8) | 164·15 (4) |
| 8 | 109·20 (8) | 140·38 (10) | 175·43 (3) |
| 9 | 113·59 (6) | 148·62 (8) | 187·61 (4) |
| 10 | 118·90 (6) | 157·83 (9) | 200·68 (4) |
| 11 | 125·14 (5) | 167·97 (8) | 214·70 (4) |
| 12 | 132·36 (5) | 179·03 (6) | (masked by Hα) |
| 13 | 140·38 | 191·02 (6) | 245·53 (2) |
| 14 | 149·45 (5) | 203·90 (5) | |
| 15 | 159·29 (3) | 217·86 (6) | |
| 16 | 170·24 (3) | (masked by Hα) | |
| 17 | 182·06 (2) | 248·20 (6) | |
| 18 | 194·79 (1) | 264·69 (5) | |
| 19 | 208·47 (0) | 282·26 (7) | |

TABLE III.

$\Delta_2F'(J)$ *Values.*

*Calculated Values are from Rosenthal and Jenkins* (l.c.).

| J | Observed R(J)−P(J) | | Calculated |
|---|---|---|---|
| | λ 6080 Å.U. | λ 6620 Å.U. | |
| 1 | .. | 11·38 | 11·62 |
| 2 | 19·29 | 19·55 | 19·47 |
| 3 | 27·19 | 27·35 | 27·26 |
| 4 | 35·00 | 34·97 | 35·05 |
| 5 | 42·91 | 42·93 | 42·83 |
| 6 | 50·60 | 50·70 | 50·62 |
| 7 | 58·34 | 58·42 | 58·40 |
| 8 | 66·16 | 66·23 | 66·18 |
| 9 | 73·93 | 74·02 | 73·96 |
| 10 | 81·73 | 81·78 | 81·74 |
| 11 | 89·53 | 89·56 | 89·51 |
| 12 | .. | .. | 97·27 |
| 13 | .. | 105·15 | 105·04 |

molecule. It is further likely that the state K at 38820 cm.$^{-1}$, discovered by Kaplan[9] is responsible for some of the perturbations. The band which involves this state is reported to possess a structure similar to the fourth positive carbon bands. Therefore it is probable that K is a singlet level.

In addition to perturbations, the Ångström and certain other bands of the CO molecule are reported to exhibit the phenomenon of predissociation.[10] Brons has recently given[11] an interpretation of this and attributes the predissociation in the Ångström bands as due to a molecular term arising out of $C(^1S) + O(^3P)$. This term can only be a triplet term which according to

TABLE IV.
*Term Differences.*

| J | λ 6080 Å.U. | | | | λ 6620 Å.U. | | | |
|---|---|---|---|---|---|---|---|---|
| | $\Delta_1F'(J)$ | | $\Delta_1F''(J)$ | | $\Delta_1F'(J)$ | | $\Delta_1F''(J)$ | |
| | R(J) − Q(J) | Q(J+1)−P(J+1) | R(J)−Q(J+1) | Q(J)−P(J+1) | R(J) − Q(J) | Q(J+1) − P(J+1) | R(J)−Q(J+1) | Q(J)−P(J+1) |
| 0 | .. | .. | .. | .. | .. | 3·83 | .. | .. |
| 1 | .. | .. | .. | .. | 7·55 | 7·81 | 5·69 | 5·95 |
| 2 | 11·37 | 11·47 | 9·13 | 8·85 | 11·74 | 11·83 | 8·95 | 9·04 |
| 3 | 15·74 | 15·40 | 12·18 | 11·84 | 15·52 | 15·49 | 11·86 | 11·83 |
| 4 | 19·60 | 19·43 | 15·18 | 15·01 | 19·48 | 19·50 | 14·86 | 14·88 |
| 5 | 23·50 | 23·24 | 18·20 | 17·94 | 23·41 | 23·38 | 17·86 | 17·83 |
| 6 | 27·36 | 27·16 | 21·12 | 20·92 | 27·32 | 27·23 | 20·91 | 20·82 |
| 7 | 31·18 | 31·00 | 24·19 | 24·01 | 31·19 | 31·18 | 23·78 | 23·76 |
| 8 | 35·16 | 34·91 | 27·23 | 26·98 | 35·05 | 35·03 | 26·81 | 26·79 |
| 9 | 39·02 | 38·83 | 30·24 | 30·05 | 38·99 | 38·93 | 29·78 | 29·72 |
| 10 | 42·90 | 42·78 | 33·25 | 33·13 | 42·85 | 42·85 | 32·71 | 32·69 |
| 11 | 46·75 | 46·66 | 36·20 | 36·13 | 46·73 | 46·67 | 35·67 | 35·66 |
| 12 | | 50·61 | | 39·18 | .. | 50·64 | .. | 38·65 |
| 13 | | 54·38 | | 42·19 | 54·51 | 54·45 | 41·63 | 41·57 |
| 14 | | 58·37 | | 45·17 | | 58·57 | | 44·61 |
| 15 | | | | 48·26 | | .. | | 47·62 |
| 16 | | | | | | 66·14 | | .. |
| 17 | | | | | | 69·90 | | 53·41 |
| 18 | | | | | | 73·79 | | 56·22 |

Kronig's theory[8] should not perturb or predissociate the singlet level $B^1\Sigma$ of the Ångström bands. Similarly, most of the other correlations that he gives indicate a direct violation of the selection rule. We believe that these predissociations, if real, have to be explained in a different way, especially in view of the very low value for the energy of dissociation which comes out by this correlation. We intend to discuss this in detail in a separate communication.†

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† This number p. 562.

# ON THE DISSOCIATION ENERGY OF CARBON MONOXIDE.

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The energy of dissociation of the CO molecule has been the subject of a discussion since some time past. Quite recently Herzberg[1] has pointed out certain objections against the low value of 8·41 volts for D (CO) given by Coster and Brons[2]. On the other hand, Schmid and Gerö[3] still more recently have suggested a much lower value of 6·9 volts for D (CO). All these various values have been based on data of rotational pre-dissociation and we have therefore thought it desirable to point out some more objections both of an experimental and a theoretical nature.

Rotational predissociation is in general recognised by an abrupt disappearance of the individual band lines. But the converse is not always true, because such a disappearance may be brought about simply by experimental conditions, *i.e.*, by factors which have nothing to do with pre-dissociation like the intrinsic intensity of the band, the method of production depending on temperature, the sensitivity of the plate, the time of exposure etc. Indeed the predissociation at 9·66 volts above the ground level obtained by Coster and Brons and on which they very definitely based the value of 8·41 volts for D (CO), has been shown to be an instance of this kind. Whereas Brons did not obtain lines higher than $J = 17$ in the three bands of the fourth positive group, which he measured, Gerö[4] obtained for the two of these bands which he measured, lines up till about $J = 34$. This significant observation not only invalidates the value of 8·41 volts for D (CO) but also strengthens our viewpoint that the other observations of decrease of intensity, which are ascribed to predissociation, might also arise from similar causes especially the one[5] found in $b^3\Sigma$. Other instances of a similar kind are the Herzberg and Ångström bands in which earlier workers[6] could only measure lines up to about $J = 25$ whereas recent work under different methods of production shows that it is possible to obtain lines with higher rotational quantum numbers. The intensity distribution especially in these bands is

furthermore complicated and rendered chaotic by a large number of extraneous lines which Coster and Brons[7] take for $CO_2$ bands, but which evidently belong to the CO bands of the system $a' {}^3\Sigma \rightarrow a^3\Pi$. Therefore such slight irregularities cannot be called abnormal and the intensity distribution of the (0, 0) Ångström band shown in the reproduced microphotometer plate[7], to our mind, requires further experimental confirmation on account of the numerous extraneous lines. Similar remarks apply to the decrease in intensity observed in the other Ångström band and the Herzberg bands[8]. It seems therefore doubtful, whether the dissociations at 11·54 and 11·08 volts are already definitely established.

Assuming, however, that some of these cases of intensity decrease come out to correspond to a dissociation of the molecule, the further questions arise, whether it is a case of real predissociation or the ordinary dissociation by instability of the molecule brought about by rotation. Only the former case means an improvement on the usual vibrational extrapolation. An example is furnished by $S_2$. The value for D ($S_2$) obtained from the interpretation of the abrupt termination of the rotational structure in two successive vibrational levels does not agree, as we have pointed out recently[9] at greater length, with the value obtained from the convergence point, whatever products of dissociation are assumed for the upper electronic term. Indeed, as far as CO is concerned, it is rather surprising that most of the various predissociations would at the same time mean a violation of the selection rule in Kronig's theory of rotational predissociation[10]. It is sometimes assumed that such a violation is observed[11] in the spectrum of $P_2$ but even here it does not appear to be definitely established because the argument is based on the extrapolated values of the energy of dissociation of $P_2$ and of excitation of P which themselves are somewhat uncertain. If, however, the interpretation in the $P_2$ molecule is correct, it can mean only an exception to the general rule, and such exceptions can hardly be so numerous as they would be in the case of CO.

Predissociation data always give an upper limit to the energy of dissociation because they involve a certain amount of kinetic energy, which may be small or great depending upon the steepness of the repulsive curve. An exact correlation of values obtained from such data to the levels of the separated system is not to be expected and hence the existence of such exact correlation does not establish a true case of predissociation. We may illustrate it by the value of 9·66 volts of Brons, which lies 1·42 volts below 11·08, and corresponds exactly to the excitation energy of the C atom but just this value of 9·66 volts has been proved to be incorrect.

Herzberg has already pointed out[1], that the energy difference of about half a volt between the two predissociations in C $^1\Sigma$ and B $^1\Sigma$ can be explained as a true difference between terms of the separated systems only in a very artificial way and is inclined to take this amount as an excess of kinetic energy. If we assume that Kronig's selection rule is strictly valid, we shall have to explain both of these predissociations by repulsive curves originating in C ($^3$P) + O ($^3$P) or C ($^1$D) + O ($^1$D) (being the next higher) because only these combinations can give rise to singlet terms. In the latter case D (CO) becomes 7·86 volts, a value which appears to be too low on account of thermochemical reasons, discussed later. In the former case 11·08 volts will represent D (CO) *plus* a certain amount of kinetic energy, whose magnitude will depend on the correct value of D (CO) itself. We believe D (CO) to be roughly 10 volts, in which case the excess of kinetic energy would be about 1 volt. Schmid and Gerö[3] report another predissociation at 9·57 in A $^1\Pi$, but details about this are not yet available and we cannot say whether our general objections against predissociation values in CO will hold good also in this case. If it is a true case, D (CO) will be about 9·5 because this predissociation takes place again in a singlet level. On this view, the excess of kinetic energy for the upper one will be about one and a half volts. This rather large amount of kinetic energy can be avoided by one or other correlations, suggested by other authors, but only at the expense of the selection rule and on the assumption, except for Herzberg, that predissociation data invariably give exact values. We prefer, however, to take this excess of kinetic energy as genuine because it is obvious, that among the 18 molecular terms arising from a combination of C ($^3$P) + O ($^3$P) quite a large number will be repulsive states. Since they are not degenerate and therefore possess varying slopes and since already a single one of them will intersect various electronic states at different internuclear distances according to their heights above the ground level, we do not see any difficulty in explaining this increasing excess of kinetic energy from level to level, according to the present interpretation.

From considerations of the existence of only one or two vibrational levels in the state $b\,^3\Sigma$, a value of D (CO) = 10·45 volts has been deduced[12]. This will be the upper limit. If the new predissociation in A $^1\Pi$ is proved, this will be reduced to 9·57 volts. A value of this order of magnitude for D (CO) is to be expected from considerations of thermochemical data on account of its intimate connection with the heat of sublimation of carbon. Herzberg has already pointed out, that the data of thermochemistry give a lower limit for D (CO). We should like to add, that also the energy of the C—H bond would be reduced following a reduction in D (CO) and S (C).

Since free $CH_3$ radicals react rather rapidly with $H_2$ to form $CH_4 + H$ the C—H bond cannot have very much lower energy[13] than D ($H_2$), which means that S (C) cannot have a much lower value than 150 Kcal/mol and D (CO) a value not much lower than 10 volts.

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7. D. Coster and F. Brons., *Physica*, 1934, **1**, 155.
8. R. Schmid and L. Gerö, *Z. Phys.*, 1935, **93**, 656; 1935, **96**, 546.
9. R. K. Asundi and R. Samuel, *Proc. Ind. Acad. Sci.*, Bangalore, 1936, **3**, 466.
10. R. de L. Kronig, *Z. Phys.*, 1930, **62**, 300.
11. A. Jakowlewa, *Z. Phys.*, 1931, **69**, 548; G. Herzberg, *Phys. Rev.*, 1932, **40**, 313.
12. J. Kaplan, *Phys. Rev.*, 1931, **37**, 1406; H. Lessheim and R. Samuel, *Proc. Phys. Soc., London*, 1934, **46**, 523.
13. K. F. Bonhoeffer and P. Harteck, *Photochemie* (Berlin), 1933.

# DISPERSION OF DEPOLARISATION OF RAYLEIGH SCATTERING.

## Part I. Fatty Acids.

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### *1. Introduction.*

Although the state of polarisation of the light scattered transversely by a variety of substances has been studied in detail by numerous investigators, comparatively little work has been done on the dispersion of depolarisation with wave-length. Some early investigations carried out by K. S. Krishnan[1] on a large number of liquids using sunlight filtered through suitable coloured glasses did not show any large dependence of depolarisation on wave-length. These measurements should be taken as only preliminary, since the incident light was not strictly monochromatic, filters used transmitting fairly wide regions of the spectrum. A few years later K. S. Krishnan and A. Sircar[2] have reported the results of the measurements on the dispersion of polarisation of the light scattered by benzene both in the liquid state and in the state of vapour. It is found that while the depolarisation factor for the liquid remains constant over a wide range of wave-length the value for the vapour increases appreciably as we proceed towards the ultraviolet.

A. F. Turner[3] has studied in detail the dependence on wave-length of the intensity and depolarisation of the light scattered transversely by liquid benzene. But no appreciable dispersion of depolarisation has been reported by him. Very recently the depolarisation of the unmodified scattered light has been investigated by S. M. Mitra[4] in carbon disulphide and benzene over a wide range of wave-length, and it is found that the depolarisation factor is independent of wave-length for these two liquids. The investigators mentioned above restricted themselves to observations with a non-associated

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[1] K. S. Krishnan, *Phil. Mag.*, 1925, **50**, 697.

[2] K. S. Krishnan and A. Sircar, *Ind. Jour. Phys.*, 1931, **6**, 193.

[3] A. F. Turner, *Inaugural Dessertation, Berlin University*, 1935.

[4] S. M. Mitra, *Zeits. f. Phys.*, 1935, **96**, 29.

liquid such as benzene. Consequently in the absence of adequate data it is not justifiable to say that the depolarisation of the tranversely scattered light is independent of wave-length. It has been observed that highly associated liquids show certain anomalies in light scattering[5]. Therefore it is not unreasonable to expect an appreciable dispersion of depolarisation in these liquids. In view of these circumstances, it was thought desirable to study the dependence of depolarisation of the unmodified scattering on wave-length in a series of associated as well as non-associated liquids. In this paper the results obtained with the first five members of the fatty acids and benzene are given.

## 2. *Experimental Details.*

The principle of the method is essentially the same as in the well-known Cornu method of measuring partially polarised light which has been very frequently used in light scattering, with this difference, *viz.*, the scattered light after passing through the double-image prism and nicol is analysed spectroscopically. A fused silica cross was used as the container for the liquid to be examined. The arms of the cross were each 3 inches long and $1\frac{1}{2}$ inches in diameter with fused transparent quartz windows fused on to their ends. The cross was connected on to a pyrex flask through a quartz pyrex seal. The liquid was distilled dust free into this cross by the usual method of Martin. Chemically pure liquids were taken for the experiment. The cross was blackened on the outside excepting for three end faces.

The light from a point-light quartz mercury arc lamp was focussed at the centre of the silica cross containing the dust-free liquid. A quartz double-image prism (optical contact) was placed in the path of the transversely scattered light and it was so orientated as to deviate the rays passing through it in a vertical plane. Immediately behind it was the nicol (transmitting the ultraviolet region also) and further behind another quartz lens which focussed the two images of the track formed by the passage through the double-image prism on the slit of the spectrograph. The slit of the spectrograph was kept rather broad. The two images were well separated, one above the other, crossing the slit and corresponded to vibrations in the scattered light which were initially vertical and horizontal respectively. The spectrograph made use of in the present experiment was a small Hilger quartz spectrograph. In this arrangement the errors arising from the polarisation effects of the spectrograph were automatically eliminated. The nicol in the path of the scattered light was so orientated that the two images

[5] I. Ramakrishna Rao, *Ind. Jour. Phys.*, 1927, **2**, 61; S. Ramachandra Rao, *Ind. Jour. Phys.*, 1928, **3**, 1; R. S. Krishnan, *Proc. Ind. Acad. Sci.*, A, 1936, **3**, 126.

of the scattered light for a particular wave-length were of equal intensity. A photograph was taken for this position of the nicol. The nicol was slowly rotated step by step through a degree on either side and a series of photographs was taken for the successive orientations of the nicol. The following six liquids have been investigated thus, *viz.*, benzene, formic acid, acetic acid, propionic acid, normal butyric acid, and isobutyric acid.

### *3. Results.*

In the case of benzene it was found that for one particular orientation of the nicol the two components of the scattered light were of equal intensity for the whole recorded spectrum. With a slight rotation of the nicol either way, the same component (vertical or horizontal as the case may be) became brighter than the other for all the wave-lengths. This clearly shows that benzene does not exhibit any appreciable dispersion of depolarisation. The depolarisation factor $\rho_u$ calculated from the nicol reading for which the two components are equal in intensity is given in Table I.

In the case of formic acid it was found that for a particular orientation of the nicol, the two components were equal in intensity for $\lambda$ 2536 A.U., whereas the vertical component was still brighter than the horizontal component for $\lambda$ 4358 A.U. Conversely for another orientation of the nicol when the two components were equal in intensity for $\lambda$ 4358 A.U., the horizontal component was brighter than the vertical component for $\lambda$ 2536 A.U. For an intermediate position of the nicol the vertical component for $\lambda$ 4358 was brighter than the horizontal component, whereas for $\lambda$ 2536 the horizontal component was brighter than the vertical component. The values of $\rho_u$ for different wave-lengths are given in Table I.

Acetic acid also exhibited a similar phenomenon. In this case it was noticed that when the nicol was so orientated as to equalise in intensity the two components for $\lambda$ 2536 the horizontal component for $\lambda$ 4358 was still brighter than the vertical component. Again when the nicol was rotated further so as to equalise in intensity the components for $\lambda$ 4358 the vertical component for $\lambda$ 2536 was brighter than the horizontal component. This shows that acetic acid exhibits a dispersion of depolarisation but in the opposite direction. The values of $\rho_u$ for different wave-lengths are given in Table I. In propionic acid also an appreciable dispersion of depolarisation was observed. Normal butyric acid did not transmit the ultra-violet region and exhibited a strong fluorescence in the visible region. Consequently no quantitative measurement of depolarisation was made. Isobutyric acid also strongly absorbed the ultra-violet region. But it did not show any appreciable fluorescence in the visible region.

TABLE I.

| λ in A. U. | 4358 $\rho_u$ % | 4046 $\rho_u$ % | 3650 $\rho_u$ % | 2967 $\rho_u$ % | 2536 $\rho_u$ % |
|---|---|---|---|---|---|
| 1. Benzene .. | 45·5 | 45·5 | 45·5 | 45·5 | absorbed |
| 2. Formic acid .. | 47 | 47 | 49 | 50·8 | 52·8 |
| 3. Acetic acid .. | 44 | 44 | 42·2 | 40·5 | 36 |
| 4. Propionic acid .. | 42 | 42 | 43·7 | 44 | absorbed |
| 5. Isobutyric acid .. | 36 | 36 | 36 | absorbed | absorbed |

*4. Theoretical Discussion.*

It is well known that the depolaristaion factor of the light scattered by the molecules in the gaseous state is a measure of their optical anisotropy, in other words, is due to the fact that the optical polarisabilities of the molecules are different in different directions. K. R. Ramanathan[6] has derived a formula for the depolarisation of the light scattered transversely by the molecules in the fluid state given by the following expression :—

$$\rho_u = \frac{6\delta}{\frac{5RT\beta n}{N} + 7\delta} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1)$$

where $\rho_u$ = depolarisation factor when the incident light is unpolarised.

R = gas constant.

T = absolute temperature.

$\beta$ = compressibility coefficient.

$n$ and N are the number of molecules per c.c. and per gram molecule of the fluid.

$\delta$ is what is called the anisotropy factor and it is given by

$$\delta = \frac{A^2 + B^2 + C^2 - AB - BC - CA}{(A + B + C)^2} \quad .. \quad .. \quad .. \quad (2)$$

where A, B and C are the optical moments induced in the molecule when it is placed in a field of unit intensity respectively along its three principal axes. For gases and vapours at low pressures which obey Boyle's law to a first approximation $\frac{RT\beta n}{N} = 1$ and consequently $\rho_u = \frac{6\delta}{5 + 7\delta}$ .. (3)

[6] K. R. Ramanathan, *Ind. Jour. Phys.*, 1927, **1**, 420.

It follows from equations 2 and 3 that if the ratio of the polarisabilities along any two axes in the molecule depends on the wave-length of the incident light wave, the optical anisotropy as well as the depolarisation factor will vary with the wave-length. Such a dispersion of optical anisotropy would be a genuine molecular property. On the other hand, if the ratio of the polarisabilities is independent of wave-length, the depolarisation factor also will be independent of wave-length.

In the case of a non-associated liquid, the depolarisation factor $\rho_u$ is given by the same equation 1 (given above). But the value of $\delta$ is given by the following[7] :

$$\delta = \frac{(A' - B')^2 + (B' - C')^2 + (C' - A')^2}{2\,(A' + B' + C')^2} \qquad .. \qquad .. \quad (4)$$

where $A' = A(1 + p_1 \chi)$
$B' = B(1 + p_2 \chi)$
$C' = C(1 + p_3 \chi)$

$p_1$, $p_2$ and $p_3$ are the constants of anisotropy of the polarisation field. $\chi$ is the susceptibility of the medium. In the case of ordinary liquids also, if the anisotropy factor depends on the wave-length of the incident light wave, the depolarisation factor will show a dispersion. From a comparison of the expressions for $\rho_u$ in the liquid state and in the state of vapour, it is seen that if the molecules in the vapour state do not exhibit any dispersion, no dispersion will be exhibited by them in the liquid state. On the other hand, if they show an appreciable dispersion in the gaseous state they may show a dispersion in the liquid state as well but to a much smaller degree.

The generalisations given above are not applicable to the case of highly associated liquids, such as liquid fatty acids. S. Ramachandra Rao[8] has studied the variations of intensity and depolarisation factor of the transversely scattered light in the case of a large number of liquids. He finds that in almost all liquids the optical anisotropy as calculated from the depolarisation values increases with rise in temperature. But in acetic acid the anisotropy decreases when the temperature is raised up to 120° C. and above that temperature, it increases in the normal way.

Very recently the variations in intensity and depolarisation factor of the transversely scattered light have been studied by the author[9] in the case of the first four fatty acids with the incident light in the three different states of polarisation, namely unpolarised, horizontally polarised and vertically

[7] C. V. Raman and K. S. Krishnan, *Phil. Mag.*, 1928, **5**, 498.

[8] S. Ramachandra Rao, *Indian Journal of Physics*, 1928, **3**, 1.

[9] R. S. Krishnan, *Proc. Ind. Acad. Sci.*, A, 1936, **3**, 126.

polarised. In the case of formic acid and acetic acid the depolarisation factor $\rho_h$ is found to be distinctly less than 1, contrary to the molecular theory of light scattering. $\rho_h$ increases with rise in temperature attaining its limiting value of unity at about 90° C. The intensity of scattering also at first diminishes with rise in temperature in these liquids. These observations have furnished for the first time definite experimental evidence for the existence of large molecular aggregates in these highly associated liquids of size not small compared with the wave-length of light. In these highly associated liquids, the depolarisation factor $\rho_u$ arises not only from the actual anisotropy of the individual scattering particles, but also from their finite size. The depolarisation factor arising from the finite size of the molecular groups will increase with decrease of wave-length. Therefore it is natural to expect an appreciable dispersion of depolarisation. The increase of depolarisation with diminution in wave-length in the case of formic and propionic acids can very easily be explained on the basis of association. In formic acid since the association is greater, the dispersion is also greater than in propionic acid. But it remains unexplained why in the case of acetic acid the depolarisation factor diminishes as the wave-length decreases.

In conclusion the author takes this opportunity to express his grateful thanks to Prof. Sir C. V. Raman, KT., F.R.S., N.L., for his kind interest in the work.

## 5. *Summary.*

The paper describes the results of measurements on the dispersion of polarisation of light scattered by benzene, formic acid, acetic acid, propionic acid and isobutyric acid. The depolarisation factor for benzene is constant over a wide range of wave-length. In the case of formic acid and propionic acid the depolarisation factor is found to increase and in acetic acid it is found to decrease as we proceed towards the ultra-violet. It is pointed out that the formation of large molecular groups in the fatty acids is probably responsible for the observed dispersion of depolarisation.

# ON THE STRUCTURE AND OPTICAL CHARACTERS OF THE NACRE IN IRIDESCENT SHELLS.—PART I.

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## *1. Introduction.*

It is common knowledge that the colours exhibited by mother-of-pearl owe their origin to the regularly laminated structure of this substance. The pioneer investigations of Sir David Brewster[1] and the more recent studies of Pfund[2] and of Lord Rayleigh[3] may be cited in this connection. These researches, however, left much ground unexplored. Much has been added to our knowledge of the structure of the nacreous substance by the work of W. J. Schmidt[4] and his pupils, an account of which is conveniently accessible in the memoir on Bivalves by F. Haas.[5] On the optical side, the recent work of Sir C. V. Raman[6] has brought to light a variety of new effects demanding explanation and which have stimulated further investigations into the whole subject.

According to Schmidt, mother-of-pearl consists of microscopically small tablet-shaped crystals of aragonite formed along the basis, the so-called platelets of mother-of-pearl, which are regularly arranged in positions parallel to the surface of the shell and are cemented together by an organic substance, the so-called conchin or conchyolin. The platelets so held together form elementary laminæ and these are in their turn superposed on one another in great numbers and cemented together by extremely thin layers of the same organic substance. The thickness of the elementary laminæ corresponds to that of the platelets of which they are composed, and is of the order of magnitude $1\mu$ but may vary between the extreme

1. For a summary, see his *Treatise on Optics*, 1853, p. 137.
2. A. H. Pfund, *Frankl. Inst. Jour.*, 1917, **183**, 153.
3. Lord Rayleigh, *Proc. Roy. Soc.*, (A), 1923, **102**, 674.
4. W. J. Schmidt, *Die Bausteine des Tierkorpers in Polarisiertem Lichte*, F. Cohen, Bonn, 1924.
5. F. Haas, "*Bronn's Klassen und Ordnungen des Tier-reichs*," Akad. Verlag., Leipzig, 1931, **3**, iii, 1–4.
6. C. V. Raman, *Proc. Ind. Acad. Sci.*, A, 1934, **1**, 567, 574, 859.

limits 0·5$\mu$ and 2$\mu$ in different species. The actual thickness of the organic layers is exceedingly small compared with that of the aragonite layers and this has been inferred by Schmidt from his observations of the cross-sections of mother-of-pearl under the highest available magnifications. Further, according to Schmidt, mother-of-pearl is an aggregate of crystals, which both in the individual elementary laminæ and also in the neighbouring ones are arranged essentially parallel to one another. This regular arrangement of innumerable single crystals is regarded as explaining the more or less complete optical homogeneity of the substance, indicated by the more or less uniform extinction and axial picture which is determined by the aggregate of the regularly arranged ultimate units. The *c* axis is normal to the elementary laminæ, and the lines of growth on the shell lie on the axial plane and are parallel to the macro-axis. (In rare cases, the axial plane and the lines of growth cross each other, and the latter then correspond to the brachy-axis.)

The granular structure of nacre led Raman[7] to infer that the individual particles in their environment should be capable of diffracting or diffusing light in a manner determined by their size, shape, orientation and grouping relatively to each other in the laminæ. Direct evidence that such diffraction effects do occur is furnished by the diffusion haloes, exhibited by a thin plate of nacre when it is held before the eye and a bright source of light viewed through it. These diffusion haloes form a unique method of revealing the structure of the nacreous substance, and a study of them led Raman to conclude that the structure of nacre is entirely different in the three great divisions of the Mollusca—namely the Lamellibranchs, Gastropods and Cephelopods, and that it also exhibits notable variations as between individual families and species. The Gastropod shells—*Turbo*, *Trochus* and *Haliotis* give haloes that form more or less complete circles. That of the Cephelopod—*Nautilus*—is of very peculiar form, consisting of two roughly circular but incomplete arcs of about 60° angle on either side of the direct beam. The bivalve shells, of which five different species were studied by him, give again quite a different type of halo, namely two spots or rather diffraction spectra, one on either side of the central diffraction disc and distinctly separated from it. Closer study reveals that though the diffusion haloes of *Trochus* and of *Haliotis* resemble that of *Turbo* in having circular symmetry, they differ strikingly in detail. Similarly, though the different species of bivalves examined show the same general type of diffusion halo, they differ considerably in detail. The size and arrangement of the crystalline particles in the laminæ can be inferred from the observed character of

7. *Loc. cit.*, pp. 859–860, 865–867.

the haloes as well as their angular dimensions. The haloes observed in the case of *Turbo* and other Gastropods indicate that the crystal particles are arranged in the plane of the laminæ without preference for any particular direction, that is with circular symmetry. On the other hand, in the Lamellibranchs, the particles are distinctly smaller in size and are evidently arranged in a manner which stimulates the lines of a coarsely ruled linear grating.

There is a close relationship between the results deduced from the observations of the diffusion haloes and those indicated by a study of the X-ray patterns of mother-of-pearl by Dr. S. Rama Swamy,[8] who examined the nacreous layer of iridescent shells using a monochromatic X-ray beam incident along various directions. From a study of these patterns, it is found that the nacreous layers of all the shells consist of aragonite crystals orientated with their *c* axes normal to the surface. But the orientations of the other two axes vary with the particular kind of shell. The X-ray diffraction patterns for Gastropod shells, like *Turbo*, *Trochus*, etc., with the rays incident normally to the laminations consist of complete circles, while with X-rays incident parallel to them a spot pattern is obtained. These results can be explained by the assumption of crystallites whose *a* and *b* axes are oriented at random, while the *c* axes are normal to the laminations. In the Lamellibranchs such as *Mytilus Viridis* and *Margaritifera Vulgaris* a spot pattern is obtained whether the X-ray beam is incident normally to laminations or parallel to them. This means that the three axes *a*, *b* and *c* exhibit specific orientation with regard to the lines of growth in these shells. In the case of *Nautilus Pompilius* the results of the X-ray analysis indicate an arrangement of twinned crystals, with a specific orientation of the *a* and *b* axes, but with a larger error than in the bivalves.

The present paper describes the results of an investigation undertaken to find whether the structure of the nacreous substance as inferred from the optical haloes and the X-ray patterns is supported by the results of more direct study of thin sections of nacre under the petrological microscope, both with plane polarised light and convergent light.

### 2. *Examination under Plane Polarised Light.*

Except a few slides which were intended for the study of the diffusion haloes, the others were ground very thin, the average thickness being about 5$\mu$. Apart from a good rub over clean chamois leather the sections were not otherwise polished. In the case of transverse sections and a few others, previous cooking in balsam for about three hours at about 80°–90° was

8. S. Rama Swamy, *Proc. Ind. Acad. Sci.*, A, 1934, **1**, 871; 1935, **2**, 345.

found necessary. The sections were prepared cut in one or another of the three perpendicular directions—namely parallel to the surface of the shell transverse to the surface, and either parallel or perpendicular to the lines of growth on it. Even the optic sections, parallel to the surface, were so cut that the lines of growth could be easily ascertained.

For studying the texture and structure of the shells, medium power objectives were generally used, while for measurements of the size of the grains, high power objectives and a micrometer-scale reading to $2\mu$ were used. For the transverse sections and some of the Lamellibranchs, oil immersion objectives (90 X) and oculars of high power (15 X) were found absolutely necessary as the sizes were of the order of $0{\cdot}4$ to $0{\cdot}5\mu$.

**Lamellibranchata.**—The following shells belonging to this family were studied : (1) *Margaritifera Margaritifera*, (2) *Margaritifera Vulgaris*, (3) *Margaritifera Lentigunosa*, (4) *Mytilus Viridis*, and (5) *Lamellidens Marginalis*. These are all fine grained shells, the individual crystals of aragonite being quite small compared to those of the members of the other two families.

Under the microscope, they appear very fine-grained (Figs. 5–7), with the crystals of aragonite in tiny platelets of extreme thinness, and all arranged parallel, so that they look like parallel sheafs or bundles of crystals laid linearly one above the other. The crystals are arranged with their vertical axes *c* all parallel to one another and normal to the lamination plane. The two lateral axes *a* and *b* of each crystal are similarly parallel to the corresponding axes of the other crystals and lie in the plane of the optic section. The crystals are all normal and untwinned. On account of the extremely fine size and parallel arrangement, no individual faces are observable in the optic sections, except the *a* (100) face which appears as fine parallel striations and along which the crystals are bound by a thin layer of conchyolin. It is this structure of the shell that acts like a ruled grating and gives rise to the diffusion halo observed by Raman.

On account of the extreme fineness in size and absence of well-developed faces in the section it is not possible to correctly assess the size of the crystals. But the distance between the striations (Figs. 5–7) gives us the distance between the two *a* faces which in turn gives us a good idea of the relative size of the crystals in the various shells. The following table gives the size in the various bivalves. The measurements were made by means of a micrometer-scale capable of reading upto $1{\cdot}6\mu$ by using high-power objectives and oculars.

| | |
|---|---|
| *Margaritifera Margaritifera* .. .. .. | 3—4$\mu$ |
| *Margaritifera Vulgaris* .. .. .. | 2—2·5$\mu$ |
| *Margaritifera Lentigunosa* .. .. .. | 2·5—3$\mu$ |
| *Mytilus Viridis* .. .. .. .. | 1·25—1·5$\mu$ |
| *Lamellidens Marginalis* .. .. .. | 2—2·5$\mu$ |

The crystals, however, are not arranged absolutely parallel. There is a slight tilting of the *a* plane, sometimes to the right, sometimes to the left, the error in orientation being different in different shells. It is about 4° to 5° in *Margaritifera Vulgaris* and slightly more in *Margaritifera Margaritifera* and *Margaritifera Lentigunosa*. Similarly the disposition of the aragonite crystals, along the different lamination planes also is not absolutely parallel. While there is no change in the direction of the *c* axes (they are all parallel to one another) there is an error in orientation of the two lateral axes *a* and *b*. This is very noticeable if one compares instead of two immediate alternate lamination planes, two which are separated by say about half a dozen. Under crossed nicols, instead of the section becoming completely dark at one position, we get small bright parallel patches here and there, which are extinguished only by turning the section slightly to the right or the left.

In *Mytilus Viridis*, the error in orientation is somewhat large—as much as 15°, not only linearly, but also transversely. It looks as though the two lateral axes are disposed of in an undulating manner, folded as it were. On account of this the optic section, under crossed nicols, presents a curious figure (Figs. 11 and 12), with alternate bands of light and shade in both the directions—the characteristic "grating structure" of microcline. In *Lamellidens Marginalis*, the error is slightly less than in *Mytilus Viridis*, but still large enough to indicate a definite tendency for the folding or undulation noticed in the latter. The section, under crossed nicols (Fig. 13), looks like a felspar crystal which has developed polysynthetic twinning, only the edges are not so straight and well defined. This is because of not only the error in orientation, but of definite tilting of the lateral axes, now to one side, now to the other.

As is known, the axial plane of aragonite is parallel to *a* (100) and it is this plane which is observable as series of parallel striations in optic sections under the microscope. On account of the regularity in arrangement of the crystals, there is a definite relationship between this plane and the lines of growth in the shell. In most of the shells it is normal to it, *i.e.*, the lines of growth are parallel to the *a* axis. In *Margaritifera Margaritifera* it is slightly inclined and in *Margaritifera Vulgaris* the axial plane makes as little as 60° with the lines of growth.

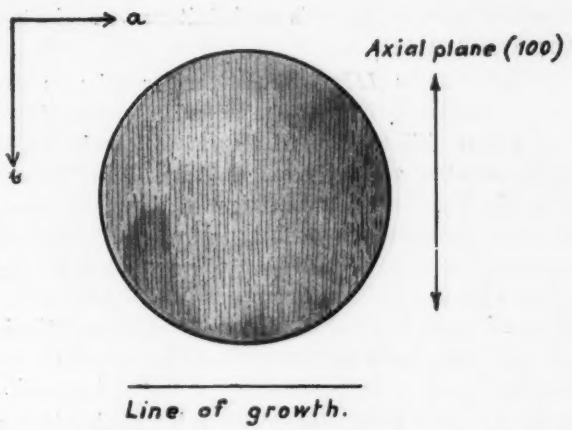


FIG. 1.—To show the orientation of the crystallographic axes and planes in the optic section of a Lamelli branch shell.

**Gastropoda.**—The following shells belonging to this great family were studied : (1) *Turbo* (sp.), (2) *Trochus* (sp.), (3) *Haliotis* (sp.), and (4) *Haliotis* (*Californian Abalone*). These are all coarse grained shells, compared to those of the previous family. Individual crystals of aragonite with well-developed faces are easily discernible under even medium power objectives. The crystals generally are normal, but good many twinned ones are found, the twinning being along the *m* (110) plane. The twins are the usual doublets, but triplets and multiple parallel series are not absent, though the former is of rare occurrence and the latter rarer still. The size of the crystals covers a wide range. In *Turbo* it is from 4 to 7$\mu$, in *Trochus* 6 to 12$\mu$ and in *Haliotis* 5 to 8$\mu$. (In an East African species of the *Haliotis* there seems to be two growths of crystals, one uniform and the other very uneven in size, the latter not being very common but clustered in places.)

The arrangement and disposition of the crystals are not the same as are observed in the members of the Lamellibranchs. The crystals are in thin tiny platelets arranged with their *c* axes parallel and normal to the elementary laminæ. While there is this regular parallelism with regard to the vertical axes of the individual crystals, there is no such orderliness in the disposition of the two lateral axes in these tiny platelets. They are thrown pell-mell with no definiteness in orientation. Under crossed nicols there is no complete extinction at any position (Figs. 14 and 15), different grains getting extinct at different times, the extinction depending upon when their vibration directions happen to coincide with those of the nicols. Thus the optic sections of these shells, under the microscope, look like a

fine grained sandstone, where there is no definiteness in orientation between the various grains of quartz.

*Haliotis, Calif. Abalone (III).*—Of the three specimens referred to by Raman[9] in his papers this is the least gorgeous in colour and the top of the nacreous layer is enamel-like. This is also more translucent to light than the others. The crystals generally are untwinned, but twinned ones are not uncommon. Unlike the other Gastropods, there is a tendency here to some arrangement, though not to such an extent as in the Lamellibranchs. Under high power, the optic section (Fig. 8), especially when just thrown out of focus, looks like a bundle of faggots tied together, each faggot representing a bundle of crystals in which the *a* axes lie along the length of the faggot. As in the other shells the vertical axis is normal to the elementary laminæ. The *b* (100) plane is parallel to the lines of growth.

**Cephelopoda.**—*Nautilus Pompilius.*—This is interesting from many points of view. It is different from the other two families not only in the outer structure of the shell, but also in the structure of its nacreous layer. It is more or less intermediate in its characters. The shell is medium grained, neither so fine grained as the Lamellibranchs nor so coarse as the Gastropods, the size of the crystals ranging from 3 to 6$\mu$. The crystals are discernible under the medium power objectives, more easily under high powers. Generally the crystals are twinned, though untwinned ones are also observed. Doublets, triplets and quadruplets, in parallel series, are quite common.

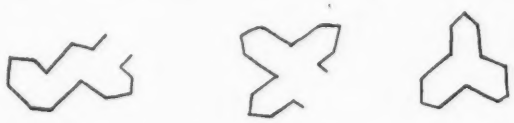

FIG. 2.—*Nautilus Pompilius.* Some of the crystal forms observed under the microscope.

Under the microscope, when observed with high power, a sort of cross-hatch structure is observed (Fig. 9), the angle between the two sets of line being about 60°. This is due to the twinning of the crystals of aragonite: the twinning plane of aragonite being *m* (110), so that the angle between two similar faces is 117°. On account of this twinning in regular order and large error in orientation of the crystals there is no complete extinction under crossed nicols. But this is quite different from that observed for the Gastropods. In the latter there is no extinction at all at any time, different grains becoming extinct at different times. But in the case of *Nautilus*, on rotation of the section through a complete range of 360°, we observe

9. *Loc. cit.*, p. 570.

at four positions maximum illumination and at four other positions, 45° from the previous ones, minimum illumination. This can be explained only on the hypothesis that the arrangement of the crystals is regular, whatever that arrangement may be.

The septum of *Nautilus Pompilius*, which is thin, is also nacreous, but not so iridescent. It is covered by a thin layer of white enamel. In contrast to the main outer shell, the septum is very coarse grained, much coarser than even the Gastropods (Fig. 16). The size of the grains ranges from 12 to 16$\mu$. The crystals are mostly twinned and the arrangement is the same as in the main shell. It is not easy to find out the relationship between the lines of growth and the crystal faces on account of the difficulty of finding out the lines of growth in mounted specimens.

### 3. *Examination under Convergent Light.*

For further study of the structure of the nacreous layers, the sections were examined under convergent polarised light. The photographs disclose a remarkable variety in the configuration of the interference figures, which disclose the arrangement of the crystals of aragonite in these shells. It will be noticed that the Gastropod shells, *Turbo*, *Trochus* and *Haliotis*, give a uni-axial figure, while the Lamellibranchs that of a biaxial figure and the Cephelopod *Nautilus* an intermediate one, a biaxial figure with a small optic axial angle (Plates XXXI and XXXII). This variety in the shape of the interference figures produced can only be explained by considering the arrangement of the individual crystals.

The cause of the interference figures, as we know, is due to the optical anisotropy and consequent double refraction of the crystals belonging to other than the isometric system. In these crystals the velocity of light and hence the refractive index is different in different directions. Rays which enter a biaxial crystal so as to travel through it in any direction other than an optic axis are split up into two rays, vibrating at right angles to each other and with different refractive indices. On account of this difference in the refractive index, a phase difference is introduced in the two rays, travelling in the same direction, and all interference phenomena observed with convergent light is due to this phase difference. The directions of maximum and minimum refractive index lie at right angles to each other and at right angles to these two is a third axis of intermediate refractive index. In uniaxial crystals the intermediate axis coincides with one of the others, so that in planes at right angles to the optic axis the refractive index is the same in every direction. In aragonite, which belongs to the biaxial group, the crystallographic *c* coincides with the acute bisectrix,

which is the direction of the fast ray. So the platelets of aragonite, we observe in the optic sections, are all perpendicular to the acute bisectrix. If we now consider a number of such platelets of aragonite, all arranged one above the other like the cards in a pack, with their *c* axes vertical and the *a* and *b* axes pointing to definite directions in the horizontal plane, then we obtain a regular biaxial crystal and a corresponding interference figure in convergent light will be obtained. For the regular arrangement leads to a complete optical homogeneity, so that it behaves like a single crystal with refractive index different in different directions. This is what actually happens in the case of Lamellibranch shells.

Let us, however, consider a different arrangement. Suppose the platelets of aragonite are all arranged one above the other with their *c* axes all vertical, but with their *a* and *b* axes pointing not to two specific directions in space but to all possible directions. If we consider any appreciable number of such platelets the resultant will be to destroy any effect of regular orientation in the horizontal plane, so that the combination will become as though it were a uniaxial type cut perpendicular to the optic axis. For the resultant of the various refractive indices of these platelets in any one direction will, for all practical purposes, on account of the random orientation, be the same as the resultant of the various refractive indices of these platelets in any other direction. In other words, the refractive index is the same in every direction in the horizontal plane. So a uniaxial figure is obtained. This is what happens in the case of Gastropod shells where there is no attempt at specific orientation in the horizontal plane.

This can also be explained analytically. It is well known that[10]

$$\tan^2 V_f = \frac{\alpha^2 (\gamma^2 - \beta^2)}{\gamma^2 (\beta^2 - \alpha^2)}$$

where $V_f$ = one half the acute optic angle for a negative crystal, in other words it is the angle between one optic axis and the fast vibration direction (**a**) which is the crystallographic *c* in aragonite. Now in the Gastropods the effect of complete random orientation of the aragonite platelets is to wipe off the difference between $\gamma$ and $\beta$ which in mathematical language might be interpreted as $\gamma = \beta$. Hence in such an arrangement $\gamma^2 - \beta^2$ will vanish so that $\tan^2 V_f$ becomes equal to zero. So $V_f$ is zero: that means the optic axes coincide with the acute bisectrix which is equivalent to the crystal being uniaxial. We also see that in these shells, on account

10. A. Johannsen, *Manual of Petrographic Methods*, 1914, p. 103.

of the definiteness in the orientation of the vertical axis, $\alpha$ remains constant while it is $\gamma - \beta$ that is changing. Since $\alpha$ is constant

$$\tan^2 V_f \text{ varies as } \gamma^2 - \beta^2.$$

In *Nautilus* due to twinning and also to a large error in orientation the effective difference between $\gamma$ and $\beta$ is reduced, though not cancelled, so that $\gamma - \beta$ is a small quantity. Hence $\tan^2 V_f$ becomes small; in other words a biaxial interference figure with a small axial angle is obtained.

*Margaritifera.*—As explained already, the arrangement of the individual crystals of aragonite is very regular in the three *Margaritifera* species examined and consequently the interference figure observed is a biaxial one (Figs. 17–19). Even here among the three species there is a slight difference in that the error of orientation is not the same, the error being large in *M. Margaritifera* and small in *M. Vulgaris*. This can also be inferred from a study of the interference figures. The optic axial angle observed in *M. Vulgaris* is the greatest while it is the least in *M. Margaritifera*.

*Mytilus Viridis.*—Here also there is a regularity of orientation as in the *Margaritifera*. Consequently the interference figure is a biaxial one (Fig. 20). But as already mentioned the arrangement here is not so perfect as in the previous shells. Due to the folding or tilting of the lateral axes, as we move the section along the lines of growth or at right angles to it, the interference figure, instead of remaining steady, as it should be

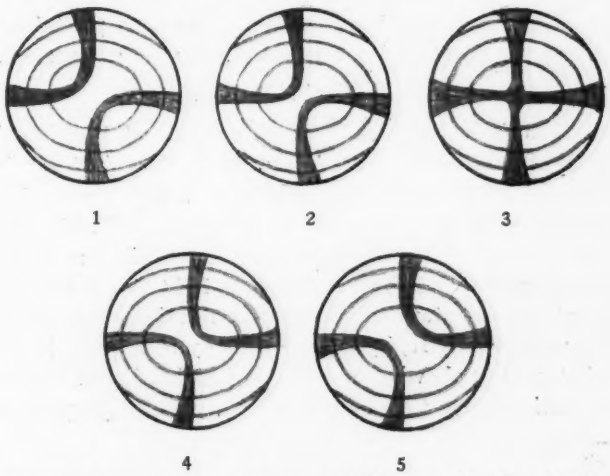


FIG. 3.—Interference figures of *Mytilus Viridis*, showing the tilt in the Axial Plane when the section is moved along the lines of growth.

if there were optical homogeneity, jumps hither and thither, while there is a change in the optic axial plane as shown by the series of figures below, with also a change in the axial angle. This change in the optic axial plane and axial angle, as the section is moved under the microscope, either along the lines of growth or perpendicular to it, cannot be accounted for except by the tilt or folding in the axes and the consequent error in orientation.

*Lamellidens Marginalis* (Fig. 21).—This also behaves very much similar to the previous shell. There is jump in the axial figure and also a change in the axial angle. Only, it is not so pronounced as in *Mytilus Viridis*. This is quite in keeping with the observations made under plane polarised light.

**Gastropods.**—All the shells belonging to this family gave under convergent light a uniaxial figure : *Turbo*, *Trochus* and *Haliotis* (Figs. 22–24). This is, as has already been explained, due to the random orientation of the platelets of aragonite.

*Haliotis, Calif. Abalone.*—There is a tendency for a biaxial figure with a small axial angle (Fig. 25). As we rotate the stage, the isogyres come and meet and then part, though on a small scale. This is because there is a tendency here in this shell, for a rough parallel grouping and not such random orientation as in the other Gastropods.

*Nautilus Pompilius.*—This gives a biaxial figure with a small axial angle (Fig. 26). The smallness of the axial angle is due to the twinning and large error in orientation of the crystals in the different laminæ.

All the photographs of the interference figures were taken in monochromatic light, the source being a mercury arc with green filter.

### *4. Diffusion Haloes.*

Raman[11] has fully explained the phenomena of the diffusion haloes observed when thin sections of the nacre are held against a bright source of light and viewed through. As explained before, nacre is composed of very thin parallel laminæ cemented together, each of which consists of a great many individual crystalline particles arranged in some kind of order. These individual particles diffract and diffuse light in a manner depending on their size, shape, orientation and grouping relative to one another in the laminæ. We may refer here, by way of analogy to a paper by Prins[12] who has given photographs showing how the diffraction haloes due to a group of particles varies with their arrangement. With lycopodium powder

11. *Loc. cit.*
12. v. J. A. Prins, *Die Naturw.*, 1931, **19**, 435.

dusted on a glass plate in such manner that the grains are very loosely and irregularly distributed, we obtain a corona with a bright central disk surrounded by alternate bright and dark rings. This pattern is progressively modified as the grains are more closely packed together, tending to a more uniform distribution. The central disk becomes less and less in intensity, until ultimately, when the grains are quite evenly and tightly packed, the corona disappears and is replaced by a diffusion halo which is separated from the image of the source of light by a dark region. The size of the halo depends on the size of the grains and wave-length of the light employed.

It has already been shown how the shape, orientation and grouping of the individual crystals observed in various nacreous shells agree generally with the conclusions arrived at by Raman by the study of the diffusion haloes. It is possible to calculate the size of the grains from the haloes assuming the nacre to form an irregular type of grating and applying the usual diffraction formula

$$d \sin \theta = n\lambda$$

where $d$ is the size of the grain which determines the distance between the successive diffracting centres.

The sections cut for the present work were thicker, about $20-30\mu$ than were used for the microscopic work. Further, both the sides were polished with the finest rouge on chamois leather, and then mounted on a slide with canada balsam and cover slip. For the source of light a mercury arc was used and the green filter for the production of monochromatic light. The lens of the camera was removed and in its place the section covered with a thin metal disc with a pin hole pierced through. By means of a suitable condenser a parallel beam of light was allowed to fall normally on the metal disc. Before photographing it was necessary to carefully orientate the specimen held in the lens panel till the complete halo was obtained on the ground glass screen, for unless the laminæ are normal to the rays the full halo is not obtained.

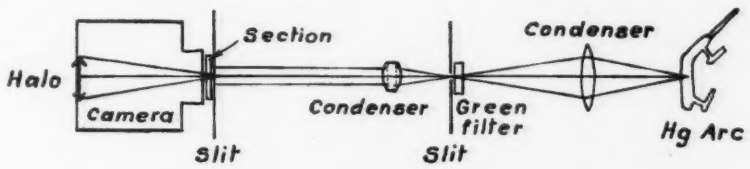


FIG. 4.—Arrangement of the Apparatus for photographing the Diffusion haloes.

| | Size as calculated from the Diffusion Halo | Size actually measured under the microscope |
|---|---|---|
| | μ | μ |
| *Margaritifera Margaritifera* .. .. | 3·2 | 3 to 4 |
| *Margaritifera Vulgaris* .. .. | 2·2 | 2 to 2·5 |
| *Margaritifera Lentigunosa* .. .. | 2·6 | 2·5 to 3 |
| *Mytilus Viridis* .. . .. | .. | 1·25 to 1·5 |
| *Lamellidens Marginalis* .. .. | 2·3 | 2 to 2·5 |
| *Turbo* (sp.) .. .. .. | 5·3 | 4 to 6 |
| *Trochus* .. .. .. | .. | 6 to 12 |
| *Haliotis* (sp.) .. .. .. | 5·6 | 5 to 8 |
| *Haliotis Calif. Abalone* .. .. | 5·6 | 5 to 8 |
| *Nautilus Pompilius* .. .. | 4·8 | 3 to 6 |

In the table above is given the size of the grains as calculated from the diffusion haloes as well as the size actually measured with the micrometer scale under the microscope. It will readily be seen that the two figures are of the same order of magnitude. Further, it was noticed that the disparity in the size of the grains had a bearing on the sharpness of the haloes; where the difference was great, the haloes were diffuse and where it was small they were sharp.

The thickness of the lamination planes and a study of the transverse sections, light absorption, etc., will form the subject of another paper.

In conclusion I wish to express my sincere thanks to Sir C. V. Raman for suggesting the above investigation and for the constant interest he took during the course of the work, and also for placing at my disposal his rich collection of beautiful shells. My thanks are also due to Dr. S. Rama Swamy for the help rendered during the preparation of this paper.

## 5. *Summary.*

This paper deals with the microscopic study of the texture and structure of the nacre of iridescent shells. These were examined under plane polarised light as also under convergent light, and measurements were made of

OPTIC SECTIONS UNDER PLANE POLARISED LIGHT.

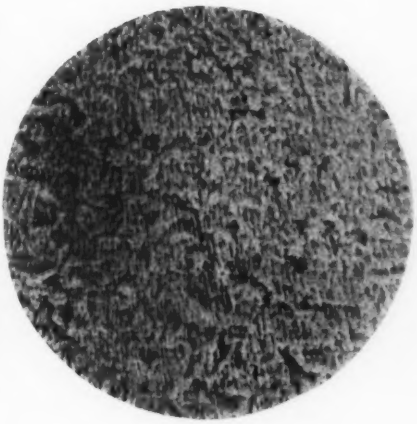

FIG. 5. *Margaritifera Margaritifera.*

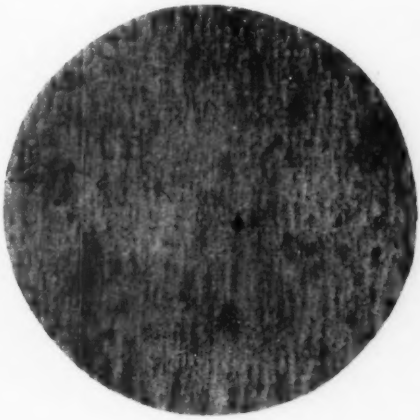

FIG. 6. *Margaritifera Vulgaris.*

FIG. 7. *Mytilus Viridis.*

FIG. 8. *Haliotis (Californian Abalone).*

## OPTIC SECTIONS UNDER PLANE POLARISED LIGHT.

FIG. 9. *Nautilus Pompilius.*

FIG. 10. Septum of *Nautilus Pompilius.*

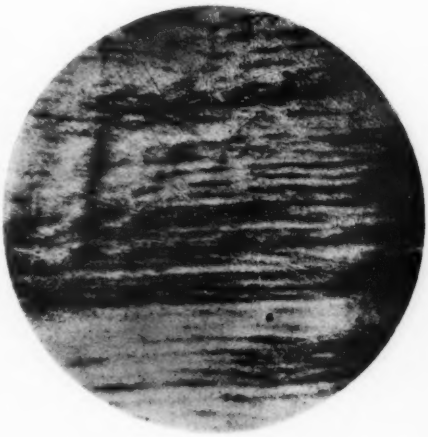

FIG. 11. *Mytilus Viridis.*
(under crossed nicols)

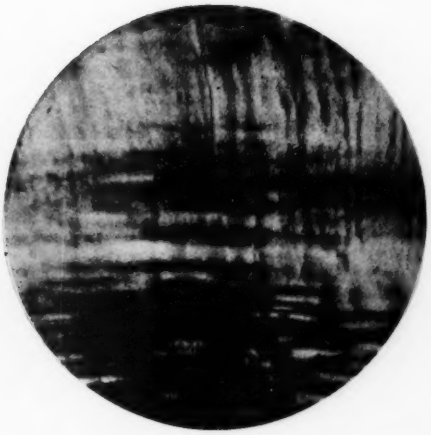

FIG. 12. *Mytilus Viridis* (thicker than 11)
(under crossed nicols)

OPTIC SECTIONS UNDER PLANE POLARISED LIGHT.

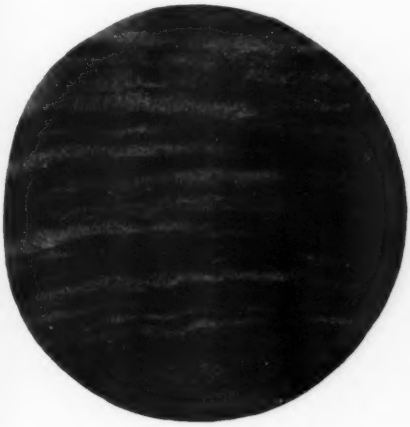

FIG. 13. *Lamellidens Marginalis.*
(under crossed nicols)

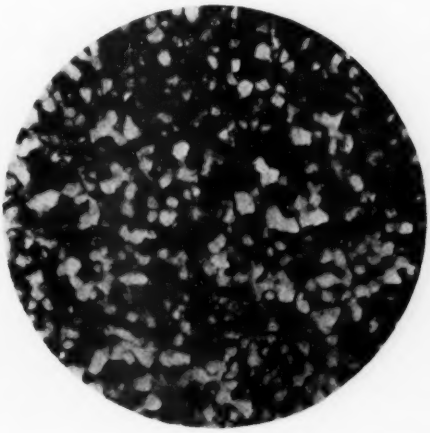

FIG. 14. *Trochus* (sp.)
(under crossed nicols)

FIG. 15. *Haliotis* (sp.)
(under crossed nicols)

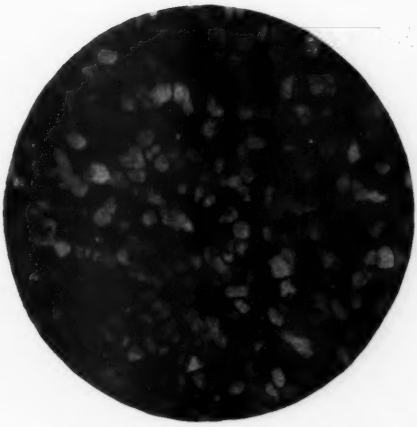

FIG. 16. Septum of *Nautilus.*
(under crossed nicols)

OPTIC SECTIONS UNDER CONVERGENT LIGHT.
(INTERFERENCE FIGURES)

FIG. 17. *Margaritifera Margaritifera.*

FIG. 18. *Margaritifera Vulgaris.*

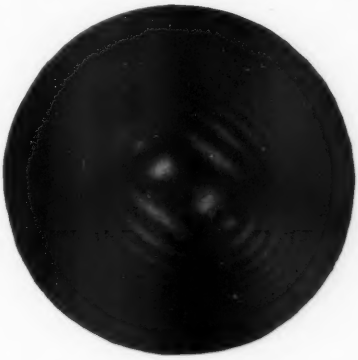

FIG. 19. *Margaritifera Lentiginosa.*

FIG. 20. *Mytilus Viridis*

FIG. 21. *Lamellidens Marginalis.*

OPTIC SECTIONS UNDER CONVERGENT LIGHT.
(INTERFERENCE FIGURES)

FIG. 22. *Turbo* (sp.)

FIG. 23. *Trochus* (sp.)

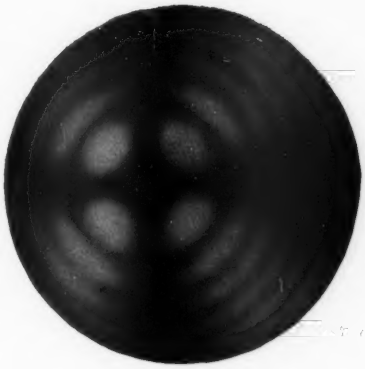

FIG. 24. *Haliotis* (sp.)

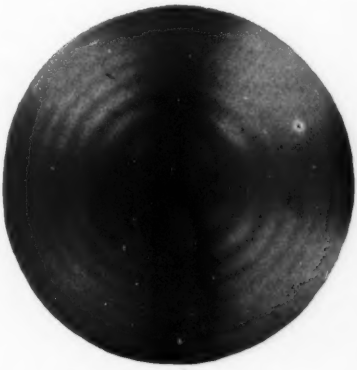

FIG. 25. *Haliotis* (Californian Abalone.)

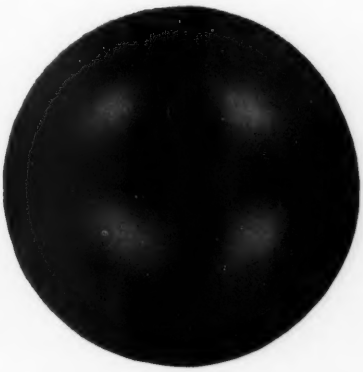

FIG. 26. *Nautilus Pompilius.*

the size of the grains under the microscope and compared with those calculated from the diffusion haloes with which they were in satisfactory agreement. The crystals of aragonite, which form the nacre in these shells, are very fine in the Lamellibranchs, medium sized in the Cephelopods and coarse in the Gastropods. Further the crystals in the Lamellibranchs are all normal and no trace of twinning is found. In the Gastropods both normal and twinned crystals are found while in the Cephelopod *Nautilus* twinned ones are the general rule. It is also found that in all these shells the aragonite crystals are in tiny platelets of extreme thinness, regularly arranged in positions parallel to the surface of the shell and held together by an extremely small quantity of cementing medium of an organic substance—the so-called conchyolin. These tiny platelets are orientated with their vertical axes *c* normal to the surface of the shell. But the orientation of the two other axes varies with the particular kind of shell examined, depending generally on the family to which it belongs. In the Lamellibranchs, where the crystals are the most orderly in arrangement, the two lateral axes are oriented in definite directions and with definite bearing to the lines of growth on the shell. In the Gastropods the crystals are randomly oriented, *i.e.*, the two lateral axes point not to two specific directions in the shell, as in the Lamellibranchs, but to all possible directions. *Nautilus* occupies an intermediate position in that the *a b* plane of the crystals has a specific orientation but with a large error. On account of this variation in the arrangement of the crystals in the three different families of the Molluscan shells the interference figure, observed with thin sections under convergent light, is also different. The Lamellibranchs give a biaxial figure, the Gastropods a uniaxial figure, while the Cephelopod *Nautilus*, which occupies an intermediate position, a biaxial figure with a small axial angle. The size of the grains as measured under the microscope is in close agreement with that calculated from the diffusion haloes. The results obtained by the microscopic examination of thin sections closely correspond with the optical observations of Sir C. V. Raman and those indicated by a study of the X-ray patterns by Dr. S. Rama Swamy.

# THE PHYSICAL IDENTITY OF ENANTIOMERS. PART II.*

## *(a)* The Rotatory Dispersion of *d*- *l*- & *dl*-forms of Iso-nitrosocamphor and their Sodium Derivatives.

## *(b)* The Differences in the Physiological Action of *d*-, *l*- & *dl*-forms of Sodioisonitrosocamphor.

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In the present communication we record the optical rotatory dispersion of iso-nitrosocamphors (*d* and *l*) in three solvents and of their sodium derivatives in water. An account of the experiments on the physiological action of the sodioisonitrosocamphors (*d*, *l* and *dl*) is also given.

Forster[1] found that two isomeric benzoyl derivatives of iso-nitrosocamphor, one yellow and another white, are formed when iso-nitrosocamphor is acted upon by benzoyl chloride in presence of sodium hydroxide. The yellow benzoyl derivative when hydrolysed by alcoholic potassium hydroxide gave colourless needles (m.p. 152–153° C.) from boiling light petroleum. Attempts to hydrolyse the colourless derivative resulted in the formation of α-camphor nitrilic acid. Later Forster[2] succeeded in getting the other isomeride of iso-nitrosocamphor melting at 114° C. from the yellow *m*-nitrobenzoyl iso-nitrosocamphor.

Still more recently a convenient method of separating the two isomerides of iso-nitrosocamphor has also been described by Forster.[3] He separates them by fractional precipitation of the isomerides from their aqueous solution of sodium salts by acetic acid.

Patterson and his collaborators[4] have studied the rotatory dispersion of isonitroso-*d*-camphor (stable variety). In 2·5 per cent. alcoholic solution,

* This work was carried out at Ravenshaw College, Cuttack.

1 *J. C. S.*, 1903, **83**, 526.

2 *Ibid.*, 1904, **85**, 904.

3 *Ibid.*, 1926, 2671.

4 *Ibid.*, 1932, 1715.

their results can be represented by the general simple dispersion equation, namely,

$$[\alpha]_{\lambda}^{28^{\circ}} = \frac{52 \cdot 4}{\lambda^2 - 0 \cdot 0857} \quad (\lambda = 4358 \text{ to } 6716).$$

We have studied the rotatory dispersion of both the stable and unstable isomerides of iso-nitrosocamphors (*d* and *l*) and of the sodium derivatives of the stable forms. Our results agree with the one-term formula. The value of rotation constant (*k*) is higher for the stable than for the unstable form.

The racemic variety of isonitrosocamphor as well as the *lævo*-form are new substances. Whereas in the case of the *lævo*-isomer both the stable (m. p. 152° C.) and the unstable (m. p. 114° C.) isomers have been isolated, only one form (m. p. 108° C.) of the racemic variety could be obtained. As this was obtained by melting the crude product which was precipitated by 20 % acetic acid from the aqueous solution of iso-nitrosocamphor (*dl*), we believe it is the stable form. The unstable form is an oil which refused to solidify.

The physical identity of the *dextro*- and the *lævo*-forms of iso-nitrosocamphor and of their sodium salts is also established, as is evident from the tables of rotatory dispersion (Tables I to VII).

*Relation between physiological action and stereoisomerism.*—The above-mentioned equality in magnitude of the rotatory dispersion of the enantiomerides is no longer observed in their biological action. It is well known that optically active antimers have different action on living matter: thus *l*-nicotine, when injected into the blood of an animal produces pain, excitation and finally death; *d*-nicotine, on the other hand, causes only a strong temporary shivering when similarly injected. With the object of studying the physiological action of *d*-, *l*- and *dl*-forms of camphor and its derivatives, one of us prepared and forwarded several of these isomers in three forms to Colonel R. N. Chopra, I.M.S., Director, Tropical School of Medicine, Calcutta. As these compounds were insoluble in water, their solutions in alcohol, glycerol and olive oil were investigated. Control experiments with the pure solvents alone showed varying degree of pharmacological effects. It was thus clear that the water insoluble isomers were not suitable for this study. The sodio derivatives of *d*-, *l*- and *dl*-iso-nitrosocamphor are soluble in water and lend themselves admirably for this work. These compounds are readily soluble in normal saline and yield clear pale yellow solutions. Colonel Chopra's report on the effect of these isomers on the blood pressure, heart *in situ* and the isolated heart is discussed below. With the sodio-derivative of *d*-isonitrosocamphor, the blood pressure is reduced, the effect being rapid

but temporary in nature. The heart beats are slowed but the muscular tone is increased in isolated heart when perfused with dilutions of 1 in 500,000 to 1 in 1,000,000. The coronary circulation is reduced. With the *lævo*-variety, under the same conditions, the fall in blood pressure is less marked, whereas in the case of *dl*-form, the effect is nil.

The rabbit's heart was stimulated with 1 in 1,000,000 dilution of the *dextro*-compound, but it was soon followed by depression, slowing of the rhythm and later on followed by irregularity of contractions. The *lævo*-variety produced only a mild stimulation with 1 in 50,000 to 1 in 100,000 dilutions, whereas under these conditions, the effect of the racemic form was nil.

When 10 milligrams of the *dextro*-compound was injected in cat intravenously, there was a fall of blood pressure. The blood pressure gradually returned to normal. This effect was practically absent in the *l*- and *dl*-isomers. The pulse rate was reduced from 200 to 160 beats per minute with the *dextro*-compound, whereas the *l*- and *dl*-forms did not produce such a marked effect.

In the case of frog's heart the action was much delayed. There appeared to be a slight stimulation when 0·1 c.c. of 1 per cent. solution of the *dextro*-compound was injected intrahepatically. The stimulation was more marked, though much delayed in occurrence. After about 10 minutes, a periodicity was noticed and there was a block in the conduction of impulses through the bundle. These effects disappeared after washing the heart with fresh saline. The *l*- and *dl*-isomers did not produce any marked effects.

The above-mentioned physiological experiments have some significance on the nature of the racemic form in solution. If the racemic form is an equimolecular mixture of the *dextro*- and *lævo*-forms, its physiological effect should be intermediate between the *dextro*- and *lævo*-forms. The evidence so far adduced shows that the physiological effects of the racemic form of the sodioisonitrosocamphor are much less marked than those of the *dextro*-compound and in some cases they are even milder than those of the *lævo*-form. It may be, therefore, inferred that racemic form of sodioisonitrosocamphor is not a mixture but a compound of the *d*- and *l*-forms. The physiological action of the *dextro*-form of sodioisonitrosocamphor is much greater than that of the *lævo*-form.

*Experimental.*

Sodium beads (8·5 g.) were immersed in dry ether (250 c.c.) in a flask, fitted with a condenser and a drying tube, and surrounded by melting ice. Camphor (54 g.) was added in small quantities and when completely

dissolved was treated in dim light with redistilled amyl nitrite (45 g.) added in small amounts. After the first few additions, the liquid became yellow. Any tendency to froth was checked by agitation and control of temperature. Subsequently the added quota was increased and the rest of the amyl nitrite was added. The reddish brown product was left in ice in a semi-dark place for 1 to 2 hours. A small quantity of solid substance appeared afterwards. In semi-darkness, ice and water were added until a reddish brown aqueous layer separated from the pale yellow ethereal solution. It is to be recalled that sodium derivative of the unstable isomeride when dissolved in water and exposed to light is transformed into the stable modification.

After removal of the aqueous layer the ethereal portion was twice washed with water. The aqueous layer was again extracted twice with small quantities of ether to remove borneol and unchanged camphor, being finally freed from ether by blowing a current of air. Dilute acetic acid (20%) was constantly added to the alkaline fluid at 0° C. in small quantities and often shaken till the volume of added acetic acid became 72 c.c. The faintly yellow precipitate was washed with ice water and ice-cold dilute acetic acid and again with ice water. Dried in air this product weighed 5 grams (m.p. 112–113° C.). The filtrate which is still yellow was transferred to a beaker and on further addition of acetic acid to it, white precipitate was thrown down (m.p. 135° C.). The precipitate (15 g.) was dried, melted and acetic acid (20%) added to it. On repeated crystallisation from acetic acid, needle-shaped white crystals (9·5 g.) were obtained (m.p. 152° C.).

The melting was done at 135° C. though Forster advises to melt the crystals at 152° C. The yield is quite good even if the crystals are melted at 135° C. and then crystallised out of 20% acetic acid.

*l*-iso-nitrosocamphor was prepared in the same manner from *l*-camphor obtained by oxidising *l*-borneol with chlorine water. The stable iso-nitrosocamphor gave m.p. 152° C., while unstable form gave m.p. 114° C.

Found : C = 65·7 ; H = 8·5 ; $C_{10}H_{15}NO_2$ requires C = 66·3 per cent. ; H = 8·28 per cent.

*Preparation of sodio-derivative of stable variety of iso-nitrosocamphor* (*d and l*).—5 g. of iso-nitrosocamphor was treated with 5 g. of sodium hydroxide in 20 c.c. water. A yellow solution resulted. The solution was concentrated on water bath. On cooling yellow crystals of sodio-derivative of iso-nitrosocamphor separated which were filtered and washed with small quantities of water, followed by ether. The yield was 4 grams.

Found : Na, 11·1, $C_{10}H_{14}O_2N$ Na requires Na = 11·31 per cent.

The yellow salt is hygroscopic, insoluble in ether and benzene and sparingly soluble in alcohol. It is extremely soluble in water and in aqueous solution reacts alkaline to litmus. Cobalt nitrate solution in water gives buff-coloured characteristic precipitate with aqueous solution of the salt, while ferrous sulphate solution gives green and nickel chloride solution white precipitate.

The racemic iso-nitrosocamphor (m.p. 108° C.) was prepared in the same manner from racemic camphor.

Found: C = 66·65; H = 7·67; $C_{10}H_{15}NO_2$ requires C = 66·3 per cent.; H = 8·29 per cent.

The sodium derivative was prepared in the same way as that of the *dextro-* and *lævo*-isomeride.

The rotatory power determinations were made in a 2-dcm. jacketed tube at 35° C. The value of $\lambda_0$ calculated from the dispersion formula is given in the tables and is expressed as $\mu$ or $10^{-4}$ cm.

TABLE I.

*Iso-nitrosocamphor (stable) in Benzene.*

$$[\alpha] = \frac{45 \cdot 56}{\lambda^2 - 0 \cdot 0921}; \quad \lambda_0 = 0 \cdot 3035$$

| *Dextro* | | | Line $\lambda$ | Calc. $[\alpha] = c$ | *Lævo* | | |
|---|---|---|---|---|---|---|---|
| Concentration g./100 c.c. | $o - c$ | Obs. $[\alpha] = o$ | | | Obs. $[\alpha] = o'$ | $o' - c$ | Concentration g./100 c.c. |
| 1·0021 | + 1·00° | + 128·3° | $Li_{6709}$ | 127·3° | − 129·1° | + 1·80° | 1·0165 |
| ,, | + 1·20 | 163·7 | $Li_{6104}$ | 162·5 | 161·2 | − 1·30 | ,, |
| ,, | ± 0·00 | 178·7 | $Na_{5893}$ | 178·7 | 180·8 | + 2·10 | ,, |
| ,, | − 1·20 | 187·6 | $Hg_{5780}$ | 188·8 | 188·7 | − 0·10 | ,, |
| ,, | − 2·20 | 219·0 | $Ag_{5468}$ | 221·2 | 220.1 | − 1·20 | ,, |
| ,, | ± 0·00 | 221·1 | $Hg_{5461}$ | 221·1 | 219·4 | − 1·70 | ,, |
| ,, | − 1·60 | 272·0 | $Cd_{5085}$ | 273·6 | 274·1 | + 0·50 | ,, |

TABLE II.

*Iso-nitrosocamphor (stable) in Ethyl Alcohol.*

$$[\alpha] = \frac{53{\cdot}74}{\lambda^2 - 0{\cdot}0740}\,;\ \lambda_0 = 0{\cdot}2720$$

| *Dextro* | | | Line $\lambda$ | Calc. $[\alpha] = c$ | *Lævo* | | |
|---|---|---|---|---|---|---|---|
| Concentration g./100 c.c. | $o - c$ | Obs. $[\alpha] = o$ | | | Obs. $[\alpha] = o'$ | $o' - c$ | Concentration g./100 c.c. |
| 1·001 | − 2·7° | + 140·3° | $Li_{6709}$ | 143·0° | −143·0° | ± 0·0° | 1·014 |
| ,, | − 0·5 | 157·4 | $Cd_{6438}$ | 157·9 | 156·1 | − 1·8 | ,, |
| ,, | − 0·3 | 179 7 | $Li_{6104}$ | 180·0 | 180·5 | + 0·5 | ,, |
| ,, | − 1·5 | 195·2 | $Na_{5893}$ | 196·7 | 197·2 | + 1·5 | ,, |
| ,, | − 2·0 | 204·6 | $Hg_{5780}$ | 206·6 | 206·0 | − 0·6 | ,, |
| ,, | + 1·2 | 241·2 | $Hg_{5461}$ | 239·8 | 239·8 | ± 0·0 | ,, |
| ,, | − 0·6 | 290·5 | $Cd_{5085}$ | 291·1 | 293·0 | + 1·9 | ,, |

TABLE III.

*Iso-nitrosocamphor (stable) in Chloroform.*

$$[\alpha] = \frac{49{\cdot}41}{\lambda^2 - 0{\cdot}0875}\,;\ \lambda_0 = 0{\cdot}2958$$

| *Dextro* | | | Line $\lambda$ | Calc. $[\alpha] = c$ | *Lævo* | | |
|---|---|---|---|---|---|---|---|
| Concentration g./100 c.c. | $o - c$ | Obs. $[\alpha] = o$ | | | Obs. $[\alpha] = o'$ | $o' - c$ | Concentration g./100 c.c. |
| 1·1015 | − 0·1° | + 136·2° | $Li_{6709}$ | 136·3° | − 134·0° | − 2·3° | 1·2015 |
| ,, | ± 0·0 | 151·1 | $Cd_{6438}$ | 151·1 | 153·0 | + 1·9 | ,, |
| ,, | + 1·2 | 174·6 | $Li_{6104}$ | 173·4 | 175·0 | + 1·6 | ,, |
| ,, | − 1·3 | 189·0 | $Na_{5893}$ | 190·3 | 188·1 | − 2·2 | ,, |
| ,, | + 1·7 | 203·2 | $Hg_{5780}$ | 201·5 | 204·2 | + 2·7 | ,, |
| ,, | + 1·2 | 235·8 | $Hg_{5461}$ | 234·6 | 235·5 | + 0·9 | ,, |
| ,, | ± 0·0 | 268·8 | $Ag_{5209}$ | 268·8 | 268·0 | − 0·8 | ,, |
| ,, | + 0·3 | 289·1 | $Cd_{5085}$ | 288·8 | 288·7 | − 0·1 | ,, |

The solution exhibited muta-rotation; the initial value $[\alpha]\ Hg_{5461} = 235{\cdot}8°$ and $[\alpha]\ Hg_{5780} = 203{\cdot}2°$ changing to 258·9° and 233·6° respectively in the course of 69 hours.

TABLE IV.

*Iso-nitrosocamphor (unstable) in Benzene.*

$$[\alpha] = \frac{34 \cdot 76}{\lambda^2 - 0 \cdot 1143}\,; \quad \lambda_0 = 0 \cdot 3380$$

| *Dextro* | | | Line $\lambda$ | Calc. $[\alpha]$ $= c$ | *Lævo* | | |
|---|---|---|---|---|---|---|---|
| Concentration g./100 c.c. | $o - c$ | Obs. $[\alpha]$ $= o$ | | | Obs. $[\alpha]$ $= o'$ | $o' - c$ | Concentration g./100 c.c. |
| 1·4816 | − 1·46° | + 102·10° | $Li_{6709}$ | 103·56° | − 103·00° | − 0·56° | 1·4915 |
| ,, | + 0·50 | 116·30 | $Cd_{6438}$ | 115·80 | 116·00 | + 0·20 | ,, |
| ,, | − 1·40 | 133·20 | $Li_{6104}$ | 134·60 | 136·00 | + 1·40 | ,, |
| ,, | + 0·94 | 150·24 | $Na_{5893}$ | 149·30 | 150·00 | + 0·70 | ,, |
| ,, | − 0·86 | 157·40 | $Hg_{5780}$ | 158·26 | 157·82 | − 0·40 | ,, |
| ,, | − 1·56 | 188·24 | $Hg_{5461}$ | 189·80 | 190·56 | + 0·77 | ,, |
| ,, | + 0·55 | 221·75 | $Ag_{5209}$ | 221·20 | 222·11 | + 0·91 | ,, |
| ,, | − 0·80 | 240·10 | $Cd_{5085}$ | 240·90 | 242·15 | + 1·25 | ,, |

TABLE V.

*Iso-nitrosocamphor (unstable) in Ethyl Alcohol.*

$$[\alpha] = \frac{34 \cdot 70}{\lambda^2 - 0 \cdot 1385}\,; \quad \lambda_0 = 0 \cdot 3721$$

| *Dextro* | | | Line $\lambda$ | Calc. $[\alpha]$ $= c$ | *Lævo* | | |
|---|---|---|---|---|---|---|---|
| Concentration g./100 c.c. | $o - c$ | Obs. $[\alpha]$ $= o$ | | | Obs. $[\alpha]$ $= o'$ | $o' - c$ | Concentration g./100 c.c. |
| 1·3916 | + 0·50° | + 109·20° | $Li_{6709}$ | 108·70° | − 108·29° | − 0·41° | 1·3915 |
| ,, | − 0·79 | 123·01 | $Cd_{6438}$ | 123·80 | 124·26 | + 0·46 | ,, |
| ,, | + 0·20 | 146·20 | $Li_{6104}$ | 146·00 | 146·50 | + 0·50 | ,, |
| ,, | − 0·50 | 167·10 | $Na_{5893}$ | 167·60 | 167·01 | − 0·59 | ,, |
| ,, | + 0·02 | 176·02 | $Hg_{5780}$ | 176·00 | 175·48 | − 0·52 | ,, |
| ,, | + 0·08 | 214·38 | $Hg_{5461}$ | 214·30 | 214·30 | ± 0·00 | ,, |
| ,, | − 1·10 | 256·20 | $Ag_{5209}$ | 257·30 | 257·01 | − 0·29 | ,, |
| ,, | − 0·59 | 284·01 | $Cd_{5085}$ | 284·60 | 284·97 | − 0·37 | ,, |

TABLE VI.

*Iso-nitrosocamphor (unstable) in Chloroform.*

$$[\alpha] = \frac{41 \cdot 24}{\lambda^2 - 0 \cdot 1044}\ ;\quad \lambda_0 = 0 \cdot 3231$$

| *Dextro* | | | Line $\lambda$ | Calc. $[\alpha] = c$ | *Lævo* | | |
|---|---|---|---|---|---|---|---|
| Concentration g./100 c.c. | $o - c$ | Obs. $[\alpha] = o$ | | | Obs. $[\alpha] = o'$ | $o' - c$ | Concentration g./100 c.c. |
| 1·5032 | + 0·60° | + 120·00° | $Li_{6709}$ | 119·40° | − 118·85° | − 0·55° | 1·5122 |
| ,, | − 0·50 | 132·50 | $Cd_{6438}$ | 133·00 | 132·80 | − 0·20 | ,, |
| ,, | − 0·80 | 153·00 | $Li_{6104}$ | 153·80 | 154·50 | + 0·70 | ,, |
| ,, | + 0·04 | 170·00 | $Na_{5893}$ | 169·96 | 169·12 | − 0·84 | ,, |
| ,, | + 0·04 | 180·00 | $Hg_{5780}$ | 179·60 | 180·00 | + 0·40 | ,, |
| ,, | + 0·05 | 213·00 | $Hg_{5461}$ | 212·95 | 213·10 | + 0·15 | ,, |
| ,, | + 1·50 | 248·50 | $Ag_{5209}$ | 247·00 | 246·15 | − 0·85 | ,, |
| ,, | − 0·55 | 266·85 | $Cd_{5085}$ | 267·40 | 267·84 | + 0·44 | ,, |

TABLE VII.

*Sodium derivative of iso-nitrosocamphor in Water (prepared from stable iso-nitrosocamphor).*

$$[\alpha] = \frac{28 \cdot 7}{\lambda^2 - 0 \cdot 1636}\ ;\ \lambda_0 = 0 \cdot 4044$$

| *Dextro* | | | Line $\lambda$ | Calc. $[\alpha] = c$ | *Lævo* | | |
|---|---|---|---|---|---|---|---|
| Concentration g./100 c.c. | $o - c$ | Obs. $[\alpha] = o$ | | | Obs. $[\alpha] = o'$ | $o' - c$ | Concentration g./100 c.c. |
| 0·435 | + 0·40° | + 98·80° | $Li_{6709}$ | 98·4° | − 98·0° | − 0·4° | 0·503 |
| ,, | ± 0·00 | 112·30 | $Cd_{6438}$ | 112·3 | 113·1 | + 0·8 | ,, |
| ,, | + 0·10 | 134·90 | $Li_{6104}$ | 134·8 | 135·6 | + 0·8 | ,, |
| ,, | − 0·90 | 152·50 | $Na_{5893}$ | 153·4 | 151·0 | − 2·3 | ,, |
| ,, | + 0·30 | 165·60 | $Hg_{5780}$ | 165·3 | 164·9 | − 0·4 | ,, |
| ,, | − 1·00 | 208·00 | $Hg_{5461}$ | 209·0 | 209·6 | − 0·3 | ,, |
| ,, | − 0·50 | 261·00 | $Ag_{5209}$ | 261·5 | 262·5 | + 1·0 | ,, |
| ,, | + 0·30 | 296·00 | $Cd_{5085}$ | 296·5 | 295·8 | − 0·7 | ,, |

No mutarotation.

# DIFFRACTION OF LIGHT BY ULTRASONIC WAVES—PART II.*

## Reflection and Transmission Phenomena.

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### *1. Introduction.*

When Lucas and Biquard, and Debye and Sears discovered at about the same time, the diffraction of light by high frequency sound waves various theories were proposed to account for the phenomenon by Debye and Sears,[1] by Brillouin[2], by Lucas and Biquard[3] and very recently by Raman and Nath.[4] Raman and Nath's theory accounts very satisfactorily for the distribution of intensities in the various orders of spectra and is in good agreement with the earlier and the more recent experimental results of R. Bär.[5] Their theory considers the amplitude and phase changes occurring in the transmitted beam, which will eventually give for the beam of light, after transmission through the medium, a corrugated wave front. This gives rise to various orders of diffraction spectra with intensities given by their formula. It also brings out quite clearly the dependence of the intensity of the various orders, on the supersonic amplitude, wave-length of light and the length of the acoustic field through which the light traverses.

But the earlier theory of Brillouin, quite different in the treatment, explained the diffraction of light by supersonic waves in liquids as due to reflection of light from striations in the medium due to the sound waves. The success of Raman-Nath's theory has put Brillouin's theory somewhat in the background. But the possibility of such reflection of light by high frequency sound waves cannot be overlooked when one is dealing with sound of very small wave-length, although we know from the work of Lord Rayleigh[6] that the intensity of such reflection of light by a liquid of varying refractive index is so small as almost to be overlooked. But under suitable conditions of experimentation, it is possible to detect this reflection. Experiments

* Part I is the paper with the same title published in the *Proc. Ind. Acad. Sci.*, 1936, **3**, 442.

carried out in this direction have proved conclusively that reflection of light does occur when the sound wave-length in the liquid is very small, quite apart from transmission occurring in all cases. This paper gives a proof of the existence of Brillouin reflections from sound waves of very high frequency travelling in liquids.

## 2. *Experimental.*

In an earlier paper,[7] we described the arrangement for a detailed study of the relationship between the angle of inclination of the quartz oscillator and the asymmetry in the diffraction spectra. We follow here the same notations with regard to the (+) and (−) orders and the same method of procedure.

The Fig. 1 of that paper holds good here also. Pronounced asymmetry is observed with greater orders on the (+) side when the quartz is turned through an angle as indicated by the arrow in the diagram.

As we expect this reflection to occur when the wave-length of sound in the medium is very small, the frequency of oscillation was increased to $20 \times 10^6$ c./s. This would give roughly a wave-length of 0·065 mm. for a liquid having the velocity of sound about 1300 m./s. This proved very satisfactory.

The steel pointer attached to the holder of the quartz oscillator, measured from rotation axis to the tip of the pointer exactly 333 mm., and a displacement, therefore, of the end of the pointer through 1 mm. on a vertical scale kept at the end, gave an angle of 10′ 18″. At times, whenever it was found necessary, the pointer was turned through even half a millimetre, so that any effect desired, such as the appearance or disappearance of any particular wave-length could be realised.

The liquids employed were toluene and butyl bromide. For the frequencies employed, these liquids gave sound wave-length of 0·0651 mm. and 0·0501 mm. respectively. The latter liquid was especially good for this work, as even the dispersion between two successive orders of spectra was greater.

With the quartz plate set at different inclinations to the incident beam, photographs of the spectra were taken on Ilford panchromatic plates. It was thought desirable to register all the wave-lengths of light of mercury arc, from 3650 Å to 5770 Å ; as then the photograph will reveal the changes accompanying each wave-length of light employed at various inclinations. This proved in the end quite satisfactory, revealing many features.

Results of observations are given in the next section.

### *3. Results.*

Figs. 1, 2 and 3 give the complete results obtained at 20 Mc. for the respective inclinations of the quartz, given on one side of the figure. Fig. 1 gives the diffraction spectra in butyl bromide for a position corresponding to the maximum intensity in the first order. Fig. 2 contains the diffraction spectra in toluene for which the sound wave-length is 0·0651 mm., while Fig. 3 is for butyl bromide, the corresponding sound wave-length being 0·0501 mm. We shall now give the results, figure by figure.

For brevity, we shall represent the prominent mercury lines 3650 Å, 4046 Å, 4358 Å, 5461 Å and 5770Å by the letters *a*, *b*, *c*, *d* and *e* respectively. This is also the notation used in the figures.

*Case* (*a*) :—*Butyl bromide* (Fig. 1) :

Observations were first made with butyl bromide, since the separation between the orders is great. Visual examination of the diffraction spectra with respect to the position of maximum intensity in the first order for 4358 Å was carried out. After careful adjustment, a photograph of the diffraction spectrum was taken, for which 4358 Å of the first order (+) was at its maximum intensity as seen visually. The two photographs in Fig. 1 relate to the two positions of the quartz oscillator, namely,

(1) when it is parallel to the beam of light, and

(2) when it is at an inclination for which the intensity of 4358 Å of the first order was a maximum. The readings were noted.

*Inclination* 0° :—The diffraction spectrum is symmetrical; *a*, *b*, *c*, *d* and *e* of the first order and *a*, *b*, *c* of the second order but very much less intense, are recorded.

*Inclination* 15′ 27″ :—This was the position for which 4358 Å line of the (+) 1 order was most intense. While generally *a*, *b*, *c*, *d* and *e* of the first order on the (+) side have greatly increased in intensity (more than twice) the same lines of the same order on the (−) side have greatly diminished in intensity. The photograph shows it remarkably enough. The second order (+) *a*, *b*, *c* have only slightly increased compared with those in 0° position, while the corresponding lines on the (−) side are completely absent. The second order *d* and *e* lines have also come out very feebly. The photograph is interesting in that the (+) first order is very intense in comparison with (−) first order, which has very nearly disappeared.

*Case* (*b*) :—*Toluene* (Fig. 2) :

*Inclination* 0° :—The photograph for 0° gives a symmetrical pattern of the diffraction spectrum, the wave-lengths *a*, *b*, *c*, *d* and *e* being very prominent. The second order for the first three lines shows very feebly.

*Inclination* 10′ 18″:—At 10′ 18″ inclination of the quartz, the second order on one side (+) for the *a*, *b*, *c* lines is bright. It is observed that the first order for these *a*, *b*, *c*, *d* and *e* lines are much brighter on the (+) side than the corresponding lines on the (−) side.

*Inclination* 20′ 36″:—For this inclination of the quartz oscillator, the intensity is a maximum for *a*, *b* and *c* lines of the second order (+), while *d* of the same order is visible. The mercury line *e* for second order has made an appearance. It can be very well noticed that the first order *a*, *b*, *c* lines on the (+) side have fallen in their intensity compared with those for inclination 10′ 18″. This position of the inclination is unique in that the mercury lines 3650, 4046 and 4358 Å of the second order are at their maximum intensity only just here. Since these lines are close together, it is difficult to say very clearly for which one of these three, this position gives maximum intensity. We shall, therefore, take them together.

*Inclination* 30′ 54″:—Strangely, while the first order (+) spectrum for the lines *a*, *b*, *c*, *d* and *e* diminished in intensity for 20′ 36″ position, the same lines for this position have strengthened, but are nonetheless less intense than those for 0° position. This is significant, for *a* and *b* of the second order have almost vanished, while *c* of the same order is only weak. The second order spectrum for *d* and *e* lines are very prominent and are at their maximum intensity here. The third order spectra for *b* and *c* have also appeared but are weaker than the corresponding lines in the second order spectrum.

*Inclination* 41′ 12″:—For this position, all the higher order spectra have completely vanished, while even the first order spectrum for the lines *a*, *b*, *c*, *d* and *e* are weak. Those on the (−) side are definitely much weaker than the ones on the (+) side.

*Case* (*c*) :—*Butyl bromide* (Fig. 3) :

*Inclination* 0°:—The diffraction spectrum is symmetrical. The first order lines are prominent, while the second order *a*, *b*, *c* are weak.

*Inclination* 10′ 18″.—The first order (+) spectral lines are in greater strength than those on the (−) side, while *a*, *b*, *c* of the second order (+) are very prominent.

*Inclination* 26′ 15″:—The second order *d* (+) is prominent. The *a*, *b*, *c* of the second order (+) are each of equal intensity. This remark is pertinent as the next para will show, where it is observed that the intensity of one is much less than the other two. (The time of exposure for this picture was much less, due to some cause.)

*Inclination* 30′ 54″:—The *a* line of the second order (+) has weakened very much compared with *b* and *c* which are strong. The *d* and *e* of the same order are fairly strong. The first order (+) for all lines are correspondingly more intense than those on the (−) side. It would appear that this is the position of maximum intensity for 4358 Å (second order +).

*Inclination* 36′ 3″:—Even the *b* and *c* of the second order (+) have weakened enormously while the *a* line has disappeared. The spectral lines *d* and *e* of this order are at their maximum intensity. This position corresponds to that of greatest intensity for 5461 (+, second order).

*Inclination* 46′ 21″:—All the second order spectral lines have vanished altogether for this position, leaving the first order, both + and −, weak.

In all the above three cases, (*a*), (*b*) and (*c*), more orders appear on that side most favourable for reflection. A reference to a similar situation can be made to the author's paper in the *Proceedings of the Indian Academy of Sciences*, Vol. III, page 442, wherein Fig. 1 exactly depicts by arrow the direction of rotation of the quartz and the part of the spectrum marked (+) where more orders are seen.

We shall discuss the significance of these results in the next section.

In addition to the results mentioned above, relating to the photographs of the spectra at different inclinations of the quartz crystal to the incident light beam, a number of visual observations were also made relating to the progressive changes in intensity accompanying the inclination of the quartz. It is thought, however, useful to give the changes in intensity for only 5461 Å (which is more sensitive to the eye than others) at various angles recorded above for both toluene and butyl bromide. The intensities given in numbers are as viewed by the author visually and though, not exact determinations, they show the changes in intensity.

*Case* (*a*) :—The relative intensities for case (*a*) are not given, for the photograph very strikingly shows the difference in intensities between the (+) and (−) first orders. While the (+) 1 order has more than doubled in intensity, the (−) 1 order has greatly weakened to probably 1/10th its value for parallel incidence of light.

*Case* (*b*) :—The table below gives relative intensities made visually for 5461 Å when toluene was used.

TABLE I.

*Relative Intensities for different Orders of Spectra for* 5461 Å *only.*
(*In Toluene.*)

| Inclination of Quartz in minutes of arc | − Order | | + Order | | |
|---|---|---|---|---|---|
| | 2 | 1 | 1 | 2 | |
| 0° | .. | 5 | 5 | 0 | |
| 10′ 18″ | .. | 4 | 10 | 1 | |
| 20′ 36″ | .. | 2 | 10 | 2 | |
| 30′ 54″ | .. | 1 | 6 | 3 | maximum |
| 41′ 12″ | .. | ½ | 3 | 0 | |

*Case* (*c*) :—Below are given visual estimates of intensities for different orders of spectra.

TABLE II.

*Relative Intensities for different Orders of Spectra for* 5461 Å *only.*
(*In Butyl Bromide.*)

| Inclination of Quartz in minutes of arc | − Order | | + Order | | |
|---|---|---|---|---|---|
| | 2 | 1 | 1 | 2 | |
| 0° | .. | 5 | 5 | 0 | |
| 10′ 18″ | .. | 4 | 10 | 1 | |
| 26′ 15″ | .. | 3 | 8 | 3 | |
| 30′ 54″ | .. | 3 | 8 | 5 | |
| 36′ 3″ | .. | 3 | 6 | 6 | maximum |
| 46′ 21″ | .. | 2 | 4 | 0 | |

*4. Discussion.*

It is well known from the work of Bragg that in the case of reflection of X-rays by layers of similar atoms, the reflection obeys the law

$$m\lambda = 2d \sin \theta$$

where $m$ is the order of the diffraction spectrum ;
$\lambda$ is the wave-length of X-rays ;
$d$ is the spacing distance ;
and $\theta$ is the angle between the incident beam and the surface (*i.e.*, 90°—angle of incidence).

Brillouin arrives at a similar formula for reflection occurring from sound wave fronts in a liquid, as modified by

$$m\lambda = 2\lambda^* \sin\theta$$

where $\lambda^*$ is the wave-length of sound,
and $\lambda$ is the wave-length of light employed.

We can verify the existence of pure reflection of light by high frequency sound waves by varying the parameters occurring in the above formula. In addition, where reflection occurs on tilting the quartz plate, the reflected beam moves through twice the angle of incidence. This affords a further verification.

The foregoing section contains results of experiments carried out in this direction. We shall now discuss the results with reference to each parameter, taking the three cases individually.

*Case* (*a*) :—*Butyl bromide* (Fig. 1) :—Since almost the entire intensity of the first order is concentrated on the (+) side for a glanzing angle of 15′ 27″, we shall consider only this case, omitting the second order, the intensity of which has not very much increased compared with 0° position. Brillouin's reflection formula requires for 4358 Å (the maximum intensity for which the crystal was rotated through) and for the wave-length of sound 0·00501 cm., a glanzing angle of 14′ 55″ for the first order. We obtained experimentally for this position an angle of 15′ 27″, calculated from a displacement of 1·5 mm. of the end of a pointer 333 mm. long. This is in good agreement with the theoretical angle of 14′ 55″ for reflection.

Further, we can calculate the angle between the reflected beam and the transmitted beam (which is, say $r$), which must equal twice the angle through which the quartz has been rotated (say twice $i$). We measure the distance $d$ between the zero order and the first order 4358 Å line as also the distance from the centre of the camera lens to the photographic plate. The respective measurements give 8·413 mm. and 958 mm. which give for the reflected beam an angle equal to 30′ 20″. The glanzing angle as given above is 15′ 27″, double of which is 30′ 54″ ($= 2i$). This is very near to 30′ 20″ ($= r$) of the reflected beam. This confirms the above remark that much light is reflected by ultrasonic waves into the first order at this inclination.

*Case* (*b*) :—*Toluene* (Fig. 2) :—Though the first order (+) is more intense than the (−) order for 10′ 18″, we shall consider only the second order reflections, as we can easily follow the intensity changes in *a*, *b*, *c*, *d* and *e* for this order.

*Second order spectrum* : (*a*) for wave-length 4358 Å :—

For this wave-length of light and for the sound wave-length of 0·00651 cm. employed, the second order reflection angle is 22′ 57″. The maximum of intensity for this line (along with 3650 Å and 4046 Å) was found to occur at 20′ 36″.

(*b*) for wave-length 5461 Å : The theoretically calculated angles occur at 28′ 47″ for 5461 Å and at 30′ 24″ for 5770 Å, while experimentally the greatest intensity for these lines was found at 30′ 52″. The agreement in these cases is satisfactory.

*Third order reflection* :—The third order reflection was observed for only two lines, namely *b* and *c*. The theoretical glanzing angles are 31′ 57″ and 34′ 26″ while at 30′ 54″ both were noticed. This is quite possible in view of the nearness of the angles to each other, and the reflection angle not being unique.

The following table gives a comparison between theory and experiment for reflection angles in toluene for the particular sound wave-length employed.

TABLE III.

*Reflection Angles* (*for 2nd and 3rd Orders of Spectra*) *for Sound Wave-length of* 0·0651 *mm.* (*In Toluene.*)

| Wave-length of light | | Reflection angle in minutes of arc | | Displacement of the pointer in mm. at a length of 333 mm. | |
|---|---|---|---|---|---|
| Symbol | in Å.U. | Theoretical | Experimental | Theoretical | Experimental |
| | *For 2nd orders* | | | | |
| *a* | 3650 | 19′ 13″ | 20′ 36″ | 1·87 | 2·0 |
| *b* | 4046 | 21′ 18″ | 20′ 36″ | 2·07 | 2·0 |
| *c* | 4358 | 22′ 57″ | 20′ 36″ | 2·23 | 2·0 |
| *d* | 5461 | 28′ 47″ | 30′ 54″ | 2·80 | 3·0 |
| *e* | 5770 | 30′ 24″ | 30′ 54″ | 2·95 | 3·0 |
| | *For 3rd orders* | | | | |
| *b* | 4046 | 31′ 57″ | 30′ 54″ | 3·10 | 3·0 |
| *c* | 4358 | 34′ 26″ | 30′ 54″ | 3·34 | 3·0 |

*Angle of the reflected spectrum* :—For 4358 Å and for second order, the angle $r$ as defined above = 45′ 20″ while $i$ read off from the inclination of the quartz is 20′ 36″ which is very nearly half $r$; similarly for 5461 Å, the angle $r$ for two orders of reflection = 57′ 4″ and this is very nearly double the angle $i$ = 30′ 54″, the position of maximum reflection for second order 5461 Å realised experimentally. Considering the conditions of experimentation, the agreement is satisfactory and proves the existence of second order Brillouin reflection.

*Case* (*c*) :—*Butyl bromide* (Fig. 3) :

First order Brillouin reflection has been considered separately under Case (*a*) and we shall mainly confine our attention to second order reflection.

*Second order spectrum* :—*for wave-length* 4358 Å :—The second order reflection for 4358 Å was found to occur in the experiments at 30′ 54″ and the theoretical reflection angle is 29′ 50″.

*For wave-length* 5461 Å :—Experimentally it was found that at a glanzing angle of 36′ 3″, the reflection maximum for second order 5461 Å occurred. The theoretically expected angle is 37′ 20″ which does not differ by much from the angle 36′ 3″. The agreement for both the wave-lengths is good.

TABLE IV.

*Reflection Angles for Two Orders for Sound Wave-length of* 0·0501 *mm.* (*In Butyl Bromide.*)

| Wave-length of light | | Reflection angle in minutes of arc | | Displacement of the pointer in mm. at a length of 333 mm. | |
|---|---|---|---|---|---|
| Symbol | in Å.U. | Theoretical | Experimental | Theoretical | Experimental |
| *a* | 3650 | 24′ 59″ | 25′ 45″ | 2·43 | 2·5 |
| *b* | 4046 | 27′ 42″ | .. | 2·69 | .. |
| *c* | 4358 | 29′ 50″ | 30′ 54″ | 2·90 | 3·0 |
| *d* | 5461 | 37′ 20″ | 36′ 3″ | 3·63 | 3·5 |
| *e* | 5770 | 39′ 30″ | .. | 3·84 | .. |

*Angle of the reflected spectrum* :—The calculations regarding $r$ and $i$ are repeated for butyl bromide for the second order for the wave-lengths 4358 Å and 5461 Å. The reflected beam for the second order 4358 was found to make an angle of 60′ 40″ ($= r$) with the parallel incident beam, while the

quartz plate was rotated through 30′ 54″ ($= i$) which is very nearly half the above angle $r$. For 5461 Å, the two angles are as given below, for the second order reflection : $r = 75'\ 20''$ ; $i = 36'\ 3''$ both determined experimentally. The agreement between theory and experiment is satisfactory.

Furthermore, we know very well that when a beam of light is reflected by layers of sound waves, as in these experiments, the angle $\theta$, at which reflection is a maximum for a particular wave-length of light ($\lambda$), is uniquely determined for a given wave-length of sound ($\lambda^*$). The formula $m\lambda = 2\lambda^* \sin\theta$ gives us further information that the smaller the $\lambda^*$, the greater is the

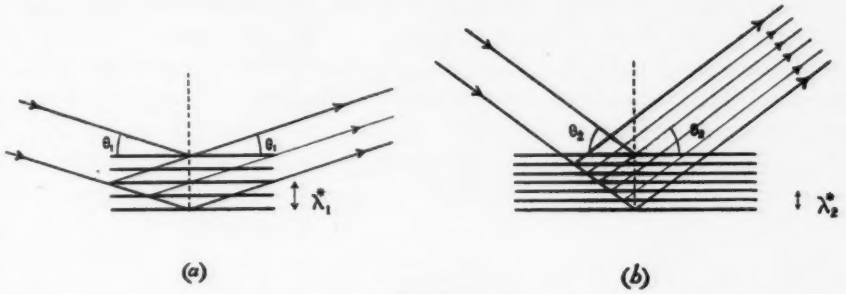


FIG. 4.

angle $\theta$ at which reflection occurs. Fig. 4 expresses diagrammatically the whole relation, $m\lambda = 2\lambda^* \sin\theta$ for the same values of $m$ and $\lambda$ in both cases pictured under ($a$) and ($b$). The thick horizontal lines indicate sound wave-fronts in the liquid, the distance between any two being half the wave-length of sound, and the oblique thinner lines indicate the path of ray. The glanzing angles are $\theta_1$ for ($a$), and $\theta_2$ for ($b$). For smaller $\lambda^*_2$ as in ($b$), $\theta_2$ is greater than $\theta_1$.

That this is so has also been verified experimentally, which again indicates that the phenomenon is due to reflection of light by high-frequency sound waves. The table below gives the glanzing angles for the quartz for second order reflection.

TABLE V.

| Wave-length of light | Wave-length of sound | $\theta$ (Experimental) |
|---|---|---|
| 5461 Å | 0·00651 cm. | 30′ 54″ |
| ,, ,, | 0·00501 ,, | 36′ 3″ |
| 4358 Å | 0·00651 ,, | 20′ 36″ |
| ,, ,, | 0·00501 ,, | 30′ 54″ |

*Intensities of the reflected light for different orders* :—We have observed in all the cases cited above that the reflection occurred successively at the first, second and third order and at no higher. For even a small rotation of the quartz above the third order reflection angle, the entire diffraction spectra completely disappeared leaving only a faint first order. It was observed in all these experiments that generally the first order reflection spectrum was most intense, the second order less and the third order feeble. We shall make a comparison of their intensities in one particular case.

Since the time of exposure was the same for all the photographs, all other conditions remaining identical, it is possible to make a comparison of intensities for various orders of reflection. The intensities of 4046 and of 4358 for any one spectrum are comparable and we give below the relative intensities for 4358 only at different inclinations where reflections of various orders occur.

TABLE VI.

*Relative Intensities for* 4358 *Line of Diffreent Orders of Reflection.*

| Order of the spectrum and nature of the phenomenon | Intensity |
|---|---|
| 1st order Transmission .. | 10 |
| 1st order Transmission and Reflection .. | 20 to 25 |
| 2nd order Reflection .. | 8 |
| 3rd order Reflection .. | 2 |

These quantitative results definitely indicate that Brillouin reflection does occur at very small wave-lengths of sound in the liquid.

It may be remarked here that S. M. Rytow[8] has made some observations on these phenomena but no photographs of reflection have been reproduced. Further, his paper was published at a time when the nature of the entire phenomenon of diffraction was not well understood, and much before the Raman-Nath theory appeared.

It is necessary to state here that the existence of reflection of light by ultrasonic waves does not create any difficulties in the Raman-Nath theory of diffraction. We have to recognise these two sets of phenomena, reflection and transmission, when we deal with the question of diffraction of light

by ultrasonic waves, and each is a distinct entity by itself. The reflection is very prominent at high frequencies, of the order of $20 \times 10^6$ c./s., while it is almost negligible or very little at 1 or 2 megacycles, so that transmission is the predominent phenomenon at the latter frequency. We must regard both of them to exist together, and the exact ratio of preponderance of one over the other will be determined solely by the wave-length of sound in the liquid ; whether it is small of the order of 0·07 mm. or less, or 0·2 mm. and greater. As examples, we shall take Fig. 1, which shows (+) 1 order very bright, while (−) 1 order has almost vanished. Probably the ratio of intensities of (+) 1 to (−) 1 will show how much is due to reflection and how much due to transmission phenomena. On the other hand, Fig. 2 in the author's earlier paper[7] shows that probably reflection takes place up to the position marked 22′, while the diffraction spectra suggest that the major phenomenon occurring is transmission. A complete theory ought, therefore, to take into account both reflection and transmission of light, with a function of the wave-length of sound and of light together, which will take proper care of these phenomena.

Here we may remark that from the identical nature of the formula connecting $\lambda$ and $\lambda^*$ derived from different standpoints by Raman and Nath from transmission, and by Brillouin from reflection, one gets further support to conclude that the nature of the diffraction is essentially a combination of both phenomena occurring together to different extents, depending on the ratio between $\lambda$ and $\lambda^*$.

The author is highly grateful to Sir C. V. Raman, Kt., F.R.S., N.L., for his interest in the work.

*Summary.*

With sound of wave-lengths 0·0651 and 0·0501 mm. in liquid, light is found to get reflected in accordance with Brillouin's formula $m\lambda = 2\lambda^* \sin\theta$. The formula is satisfied with different values for $m$, $\lambda$ and $\lambda^*$. Further, confirmation is obtained by the verification of the relation between the incident and the reflected angles, when the reflected beam moves through twice the angle of rotation of the reflecting surface. Photographs of reflection of the first, second and third orders for some prominent mercury lines are reproduced. It is made out clearly that transmission (Raman-Nath's theory) and reflection (Brillouin's theory) are two separate phenomena, superposed on each other, in the case of diffraction of light by high-frequency sound waves. Remarkably enough, the treatment for diffraction by both the methods leads to the same formula, which enhances the difficulty of separating out the intensities due to each cause.

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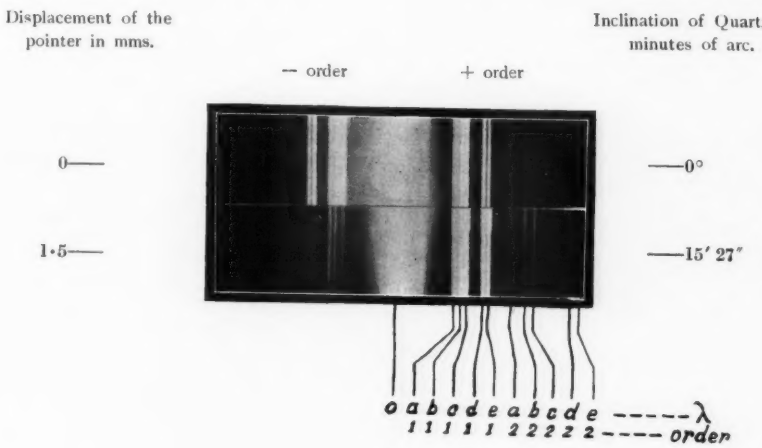
Displacement of the pointer in mms.
Inclination of Quartz in minutes of arc.
— order
+ order
0
1·5
0°
15′ 27″
o a b c d e a b c d e ----- λ
1 1 1 1 1 2 2 2 2 2 ---- order

FIG. 1.

Diffraction Spectra in Butyl bromide at 20 Mc.

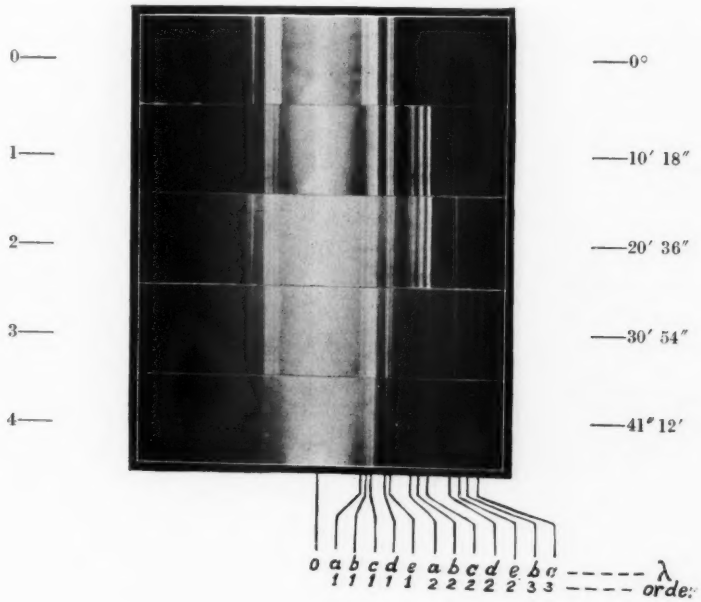


FIG. 2.

Diffraction Spectra in Toluene at 20 Mc.

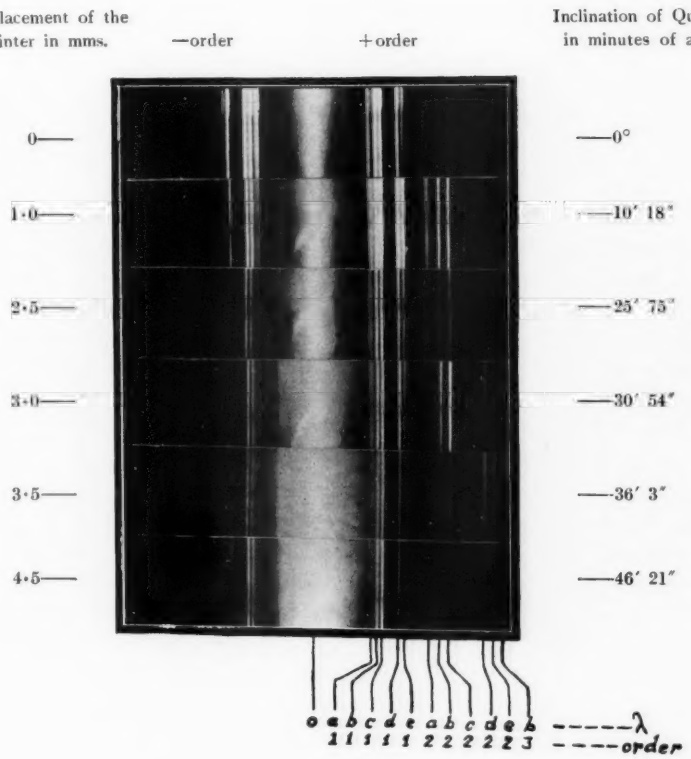


FIG. 3.

Diffraction Spectra in Butyl bromide at 20 Mc.

In Figs. 1, 2 and 3, the letters represent the wave-lengths of light. *a* for 3650Å; *b* for 4046Å; *c* for 4358Å; *d* for 5461Å and *e* for 5770Å.

# DOPPLER EFFECT IN LIGHT SCATTERING IN LIQUIDS.

## Part III. Polarisation of Light Transversely Scattered by Formic and Acetic Acids.

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

A previous communication[1] by the author described observations on the state of polarisation of the spectral components of monochromatic light transversely scattered by liquids. The scattered light was examined with the aid of the Fabry-Perot etalon in conjunction with a Füess spectrograph and some rather surprising results were obtained. It was found that while the two Brillouin (Doppler) components were completely polarised as is to be expected theoretically, the central undisplaced line was also apparently completely polarised. In all the three liquids examined (carbon tetrachloride, toluene and carbon disulphide), no rings whatever could be distinguished on the continuous background when the Fabry-Perot pattern was photographed through the Nicol with its plane of vibration axis perpendicular to the position in which the rings are seen most clearly. This appeared at first sight very surprising in view of the fact that the polarisation of the total unresolved scattered light observed transversely is imperfect to the extent of 46% in toluene and 62% in the case of carbon disulphide. This apparent paradox is resolved if we assume that the depolarised part of the scattered light appears only in the continuous spectrum or wings on either side of the Rayleigh line and that the central undisplaced component arises from individual molecules capable of free rotation. The latter assumption would give us a central undisplaced component which is almost completely polarised even in the case of highly anisotropic molecules. Considering the case of carbon disulphide for example, the light scattered by individual molecules should show a depolarisation of the order of only 11% but if the molecules are free to rotate the depolarised part would mostly appear in the P and R branches and only a small part of it in the Q branch. The Q branch in the light scattered by liquids would thus, unless

[1] B. V. Raghavendra Rao, *Proc. Ind. Acad. Sci.*, 1935, **2**, 236.

the molecules are highly anisotropic and are restricted from rotating, be more or less completely polarised. These considerations indicate that in the depolarised part of the light scattered by liquids, the undisplaced spectral line, if present at all, should be extremely weak, and that the whole of the depolarised light appears in the continuous spectrum of altered wave-length.

The present investigation was undertaken with the object of re-examining the same problem somewhat more carefully. It was thought desirable to repeat the work using finer slit widths so as to minimise the superposed continuous spectrum which tends to suppress the visibility of the spectrally well-defined parts of the scattered light. Further, it appeared desirable also to examine the case of highly associated liquids like acetic and formic acids, in which there is already some evidence available that molecular rotation is greatly hindered.[2,3,4]

*Results.*

The three typical non-associated liquids—carbon tetrachloride, toluene and carbon disulphide—were re-examined using the finest slit widths possible, and the results obtained were found to be in agreement with those previously reported, *i.e.*, all the three spectral components observed in the spectrum of the scattered light appeared only in the vertical vibration, *viz.*, were completely polarised. In the case of the highly associated liquids—formic and acetic acids—, however, it was found that in the horizontal vibration, the scattered light showed a feeble component in the position of the central undisplaced line. The appearance of this component is probably very significant in relation to the investigations of Venkateswaran,[2] Bhagavantam[3] and Rousset[4] already cited, who found that the depolarisation of the scattered light when measured spectroscopically with fine and narrow slits does not differ so greatly in the case of highly associated liquids like formic and acetic acids as in non-associated liquids. Further, R. S. Krishnan[5] has reported recently optical evidence, also based on depolarisation measurements, which indicate the presence of large clusters of molecules in these liquids. If such large clusters are present which do not rotate or oscillate freely and which depolarise the light by reason of their anisotropy of shape or structure, we should expect the Q branch of the scattered radiation, *i.e.*, the central undisplaced component, to show an appreciable

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[2] S. Venkateswaran, *Phil. Mag.*, 1932, **14**, 258.

[3] S. Bhagavantam, *Proc. Ind. Acad. Sci.*, 1935, **2**, 63.

[4] A. Rousset, *C. R.*, 1933, **197**, 1033.

[5] R. S. Krishnan, *Proc. Ind. Acad. Sci.*, 1936, **3**, 126.

degree of depolarisation. This is the result actually observed with the Fabry-Perot etalon. We may thus infer from the observed results that in formic and acetic acids, non-rotating clusters of molecules are present which depolarise the scattered light to an appreciable extent without changing its wave-length.

In conclusion, the author wishes to express his grateful thanks to his professor Sir C. V. Raman, for his kind interest in this work.

*Summary.*

The present work deals with the study of the state of polarisation of the three components observed in the spectrum of monochromatic light scattered by liquid formic and acetic acids, when examined with a Fabry-Perot etalon. It is noticed with these liquids that the central undisplaced component of the triplet observed on analysing the transversely scattered light spectrographically with a Fabry-Perot etalon shows an appreciable degree of depolarisation, differing in this respect from non-associated liquids like carbon tetrachloride, toluene and carbon disulphide, in which the central component is unobservable in the horizontal vibration of the transversely scattered light. There is thus an indication of the presence of large non-rotating or immobile clusters of molecules in these liquids which depolarise the scattered light.

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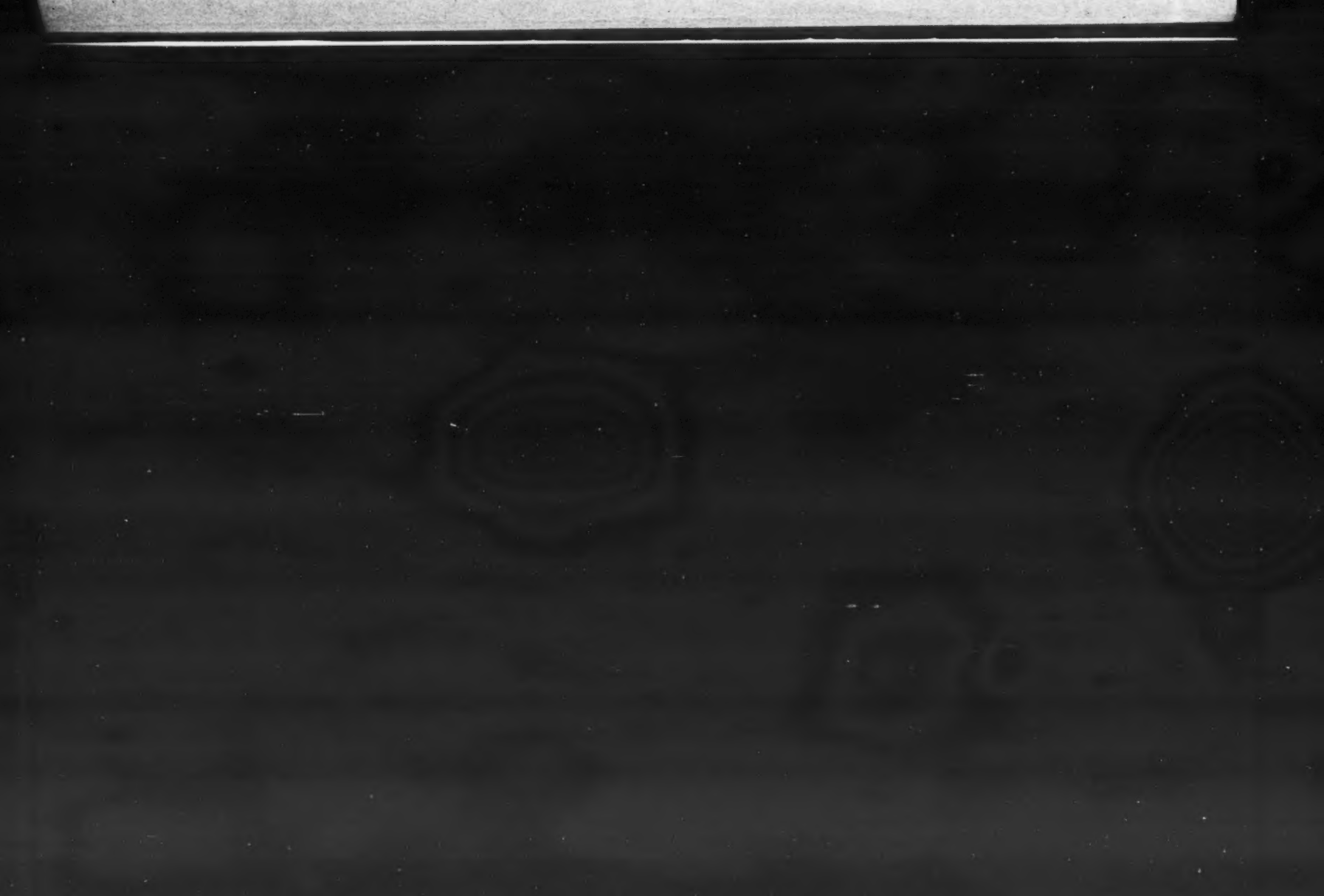

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